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# *Organic Analytical Reagents*

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VOLUME THREE

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BY

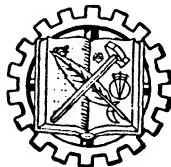
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TO MY FATHER

whose clear vision and deep understanding have contributed so much to the preparation of this work.



## PREFACE

Since the earliest days of analytical chemistry, organic reagents have been employed in various ways to facilitate the detection and determination of chemical substances. Only during the past two or three decades, however, have these compounds been used extensively in analytical procedures. At present they are rapidly gaining in popularity because of their greater sensitivity and specificity as compared to inorganic reagents, and also because of the greater convenience with which they may be employed in many analytical procedures.

The principal purpose in preparing this book has been to assemble in one place a description of all organic compounds used in the analysis of inorganic substances, and to present a discussion of the methods employing these reagents.

The information used in this book is taken from all publications appearing prior to January 1, 1946. Due to conditions resulting from the war, foreign journals have been delayed or prevented from reaching the United States, and in consequence much of the material contained in the more recent publications has been taken from *Chemical Abstracts*. For this reason, not all articles published before January 1, 1946, have been reviewed. The chemist who uses this book in reviewing the literature may, however, be guided by this principle: that all articles appearing in *Chemical Abstracts* up to and including 1945, as well as all original journals available to this date, have been included.

References to the literature have been made so as to indicate, at least to some extent, the subject matter of each. Thus the chemist who wishes to use a certain reagent for a given purpose has available a comment on almost every article that has been written on the subject and, in addition, the reference to the original publication in the event he wishes to consult this source. In this connection, it may be helpful to note that bibliofilm or photostat copies of articles appearing in most chemical journals can be secured at moderate cost from the United States Department of Agriculture Library, Washington, D. C.

Many obviously inferior reagents and methods are included since the treatment of the subject is intended to be complete. The inclusion of inferior methods is justified because of two considerations: in the future no time need be lost in attempting analytical methods that in the past have been demonstrated as unsatisfactory; and further, an inferior method may, with suitable modifications, be made useful for certain purposes.

In order to promote a more comprehensive study and a wider use of organic compounds in inorganic analysis, methods have been included for the preparation of most compounds listed in the book. For most substances, several methods appear in the literature and, in selecting the one to be included, the author has been guided by the principle that it be the most adaptable in the average chemistry laboratory. It should be stated that only a few of the methods of synthesis described have been used by the author, and undoubtedly some may prove unsatisfactory. Consequently, any information regarding better methods is earnestly solicited.

The primary aim of this book has been to collect in one place all information relating to the analytical uses of a given compound, and this principle has been adhered to regardless of structural characteristics or analytical functions. In a classification based on functions alone, many compounds would necessarily appear in different sections. For example, benzidine is used as a reducing agent, a basic salinogenic compound and in diazotization and coupling reactions for nitrite. Further, any classifications based upon functional groups present in the organic molecule would be somewhat arbitrary, since many compounds possess more than one group which affects their chemical reactions. The plan finally adopted calls for the complete treatment of each compound in one section, since any disadvantage resulting from this lack of regard for function and structure is believed compensated by the convenience of localization of information. In general, chemically related compounds are grouped together in so far as this is practicable; thus, the alcohols, amines, acids, oximes, arsonic acids, etc., form separate sections. It must be emphasized that owing to the diverse character of the reagents used in analytical procedures the associations of these substances in separate sections of this book may be somewhat debatable from the purely chemical point of view, but the plan used here seemed to be the most practicable that could be devised by the author. Although this scheme may separate such substances as reducing agents or oxidizing agents through widely scattered parts of the book, every reference to a particular reagent will be found in the section devoted to that compound.

The author is painfully aware of the many inconsistencies and ambiguities which appear in various parts of this book. Contradictory claims made by various authors are purposely included in order that the analyst may properly evaluate their merit through additional research. Many vague descriptions of methods and procedures are presented simply because the original sources themselves are not clear. Frequently, too, in translations or in abstracts errors have been discovered, which indicates too clearly that many more must certainly have escaped notice. The possibility of any error, or incompleteness of description has not prevented inclusion of certain important material, since such omissions would lead to incomplete coverage of some topics. The author also realizes that he must accept the responsibility for many mistakes, and he earnestly hopes that these will be communicated to him.

Another source of error has appeared in many publications: due to the character of chemical nomenclature, often there has been some doubt as to exactly what compound is referred to in certain discussions. This is especially true of the dyes, but is true also of certain other compounds. Every effort has been made to see that these references have been properly evaluated.

*Indianapolis, Ind.*  
August, 1946

F. J. W.

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And finally, no thanks can adequately repay the patient self-denial of his wife and sons, who have spent altogether too many months without the companionship and associations which in normal times they have so much enjoyed.

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# Part I

HETEROCYCLIC NITROGEN COMPOUNDS



# CHAPTER I

## PYRIDINE AND ITS DERIVATIVES

### PYRIDINE

$C_5H_5N$

Mol. Wt. 79.10

Beil. Ref. XX, 181.

**Use:** Detection of antimony, arsenic, cadmium, chlorate, chromate, cobalt, copper, cyanate, gold, dichromate, halogens, lead, manganese, mercury, nickel, perchlorate, permanganate, persulfate, platinum metals, phosphorus, rhenium, silica, silver, sulfur, thallium, thiocyanate, thiosulfate, vanadium, and zinc.

Determination of antimony, aluminum, bismuth, cadmium, cerium, chlorate, chromium, cobalt, copper, cyanate, cyanide, germanium, halogens, lanthanum, lead, lithium, manganese, mercury, neodymium, nickel, phosphorus, praseodymium, silica, tellurium, thiocyanate, thorium, uranium, titanium, zinc and zirconium.

Pyridine is a colorless liquid which possesses a characteristic disagreeable odor. It boils at  $115-116^{\circ}C$ . and has a sp. gr. of 0.9780. It is miscible with water in all proportions, giving a very weakly basic solution ( $K = 2.3 \times 10^{-9}$  at  $25^{\circ}C$ .). It is also miscible with alcohol and ether and many other organic liquids.

**Detection of copper.** An insoluble compound is formed when a neutral solution of a thiocyanate and a few drops of pyridine are added to a neutral solution of a copper salt. This compound corresponds in composition to the formula  $[CuPy_2](CNS)_2$ , in which pyridine is indicated by the symbol Py. This reaction has been used by Spacu<sup>1</sup> as a sensitive test for copper and for the thiocyanate ion. Pyridine should be added to the solution to be tested before the thiocyanate, since otherwise a dark precipitate of copper thiocyanate is formed in concentrated solutions. By means of this reaction copper can be detected at a concentration of 1:300,000, and thiocyanate at a concentration of 1:50,000. The sensitivity of this reaction can be increased to the point where copper can be detected at a concentration of 1:800,000 by shaking the reaction mixture with several drops of chloroform, in which the copper compound dissolves with the formation of an emerald-green coloration.

Korinskii<sup>2</sup> has used this reaction to detect copper, iron and cobalt which are present in the same solution. Iron occupies the lowest portion, copper the middle portion and cobalt the upper portion of a piece of filter paper which has been immersed in the solution containing the three ions. In this way it is possible to detect  $1\gamma$  of ferric iron in 0.2 ml. of solution in the presence of  $500\gamma$  of copper. Cobalt does not interfere. Eight  $\gamma$  of copper can be detected in the presence of  $200\gamma$  of iron.



Martini <sup>4</sup> and Dubsky <sup>3</sup> have described many tests for cations which involve the formation of well-developed crystals in the presence of pyridine or quinolone thiocyanate.<sup>156</sup> These reactions are used for the microchemical identification of copper and many other metals. The copper compound with pyridine and ammonium thiocyanate corresponds in composition to that originally prepared by Spacu.<sup>1</sup>

Dobbins and Gilreath <sup>164</sup> have precipitated as a group in a systematic scheme of analysis the metals, copper, zinc, nickel, cobalt and cadmium as the pyridine thiocyanate complexes. Briggs <sup>5</sup> and Parravano and Pasta <sup>6</sup> have prepared and studied a number of compounds formed by allowing the solutions of metallic salts to react with pyridine and dichromates. A number of these are difficultly soluble and possess recognizable crystal forms, and may be used for the micro-detection of cations from which they are formed. Korenman <sup>7</sup> has used this reaction for the microdetection of copper.

**Procedure.** Place a drop of the solution to be tested on a microscope slide and add a few drops of a cold saturated solution of potassium dichromate. Expose the drop to pyridine vapor and rub with a glass rod, and again treat with pyridine vapor. If the solution is very dilute, repeat the rubbing and treatment with pyridine. By means of this reaction, as little as 0.1γ of copper can be detected by identifying under the microscope the crystalline precipitate of  $[\text{CuPy}_4]\text{Cr}_2\text{O}_7$ .

Zwikker's reagent, which is prepared by mixing 4 ml. of 10 per cent copper sulfate solution, 1 ml. of pyridine, and 5 ml. of water, gives characteristic crystalline precipitates with perchlorates, persulfates, thiocyanates, chromates and permanganates. Wagenaar <sup>3</sup> has used a modification of this reaction as a very sensitive microchemical test for copper. He has used a few drops of a 1:10 pyridine-water mixture in N potassium permanganate as the copper reagent. This test is very sensitive.

**Determination of copper.** *Gravimetric determination:* Spacu and others <sup>9, 10, 11, 12, 13, 154</sup> have determined copper gravimetrically by precipitating as the insoluble pyridine thiocyanate complex,  $[\text{CuPy}_2](\text{SCN})_2$ . Precipitation is quantitative, and the complex can be washed, dried and weighed as such, or ignited to copper oxide. The following procedure has been proposed by Spacu and Dick:<sup>10</sup>

**Procedure.** To 75-100 ml. of the copper solution, containing not more than 0.05-0.08 g. of copper, add 8-20 drops of pyridine, or a sufficient quantity to cause the formation of an azure blue color in the solution. The pyridine should be added rapidly to prevent the appearance of a turbidity. Add 0.5 g. of ammonium thiocyanate. Stir well and filter into a filter crucible. Transfer the precipitate quantitatively to the filter with some of the filtrate. A wash solution prepared by dissolving 3 g. of ammonium thiocyanate and 3 ml. of pyridine in 1 liter of distilled water may be used for this purpose.

Wash the precipitate 6-8 times with a solution prepared as follows: dissolve 0.5 g. of ammonium thiocyanate in a mixture of 800 ml. of 95 per cent alcohol,

192 ml. of water and 8 ml. of pyridine. After the last washing, remove the last traces of the wash solution as completely as possible with strong suction and by rinsing 2-3 times with 1-2 ml. portions of absolute alcohol containing 2 drops of pyridine per 10 ml. Finally, wash the precipitate with ether containing 2 drops of pyridine per 20 ml. Suck dry, and allow the crucible and contents to stand 10 minutes in a vacuum desiccator over  $P_2O_5$ . The precipitate may be dried in an oven for 20 minutes at 40-45° C. Weigh as  $[CuPy_2](SCN)_2$ . The factor for copper is 0.18817.

Hiltner<sup>159</sup> has used this method for the determination of copper in fabrics.

A micromethod has been based on the method described above. In this procedure the copper complex is extracted with chloroform, and the solvent is then removed in a vacuum desiccator over  $P_2O_5$ . The formula pure compound is obtained.

**Separation of copper and mercury.** Spacu<sup>14,15</sup> has proposed a method for the separation and determination of copper and mercury. This depends upon the fact that copper reacts with thiocyanate in the presence of pyridine to form an insoluble green precipitate of  $[CuPy_2](CNS)_2$ , whereas the mercury salt with similar treatment yields the water soluble  $HgCl_2(SCN)^-$  ion. The following procedure may be used for the separation:

**Procedure.** Dilute the solution to be analyzed to about 150 ml., and heat to boiling. Add an excess of pyridine until the solution possesses a distinct blue color, and add about 10 times as much solid ammonium thiocyanate as the original weight of the sample. Shake or stir vigorously. Allow to stand for one hour and filter, and wash with a cold solution of 5 g. of ammonium thiocyanate and 5 ml. of pyridine per liter. Dry the precipitate at 140-150° and then ignite and weigh as CuO.

If the original solution contains considerable nitric acid, evaporate to dryness and dissolve the residue in a little dilute nitric acid. If the first precipitate of copper is pulverent because of the use of too little pyridine, dissolve in nitric acid and reprecipitate by adding more pyridine.

**Separation of zinc and copper.** Copper and zinc may be separated by a procedure depending upon the precipitation of copper in the presence of zinc by means of pyridine and ammonium thiocyanate.<sup>16</sup>

**Procedure.** Neutralize the solution to be analyzed with ammonium hydroxide and add 5-10 drops of 0.1 N ammonium thiocyanate and 5-6 drops of pyridine. Heat to boiling to dissolve the zinc compound, and add 150 ml. of cold water. Collect the green precipitate of  $[CuPy_2](SCN)_2$  in a filtering tube, wash with a dilute solution of ammonium thiocyanate and pyridine, and then ignite to copper oxide and weigh. Zinc may be recovered by evaporating the filtrate to 10-12 ml. and adding more pyridine. The zinc precipitate is collected by filtration, washed, ignited, and weighed as ZnO.

**Separation of copper from lead.** Dick and Radulescu<sup>17</sup> have modified the original procedure of Spacu for the gravimetric determination of copper,

which is based upon the precipitation of copper with pyridine and thiocyanate, by using pyridine and sodium benzoate as the precipitant.

**Procedure.** Add pyridine to 40-50 ml. of the copper solution until a slight excess is indicated by the appearance of an azure blue color. For 0.1 g. of copper, about 20-25 drops of pyridine is sufficient. Then add 3 g. of sodium benzoate dissolved in 20-25 ml. of water. This causes the formation of insoluble, blue  $[\text{CuPy}_2](\text{C}_6\text{H}_5\text{CO}_2)_2$ . Filter and wash with a solution of 1.5 g. of ammonium benzoate and 1 ml. of pyridine in 100 ml. of water. Dry, ignite and weigh as  $\text{CuO}$ .

By adding 2-3 g. of ammonium acetate to the mixture in which the precipitation is carried out, copper may be precipitated in the presence of lead; thus, by using sodium benzoate and pyridine as precipitants, copper can be determined in the presence of lead. Good results are claimed for this procedure.

**Separation of copper from manganese.** Copper may also be determined gravimetrically by precipitation with pyridine and an alkali dichromate. This method is not quite as sensitive as that based upon precipitation as the pyridine thiocyanate complex, but it provides an excellent means for separating copper from manganese. The following procedure is taken from the work of Spacu:<sup>18</sup>

**Procedure.** To 100-150 ml. of neutral or slightly acid solution containing about 0.03 g. of copper, add 0.5 g. of ammonium nitrate and an excess of pyridine. Heat the mixture to 30-40° C., and add a cold concentrated solution of an alkali dichromate. On cooling, dark green crystals of  $[\text{CuPy}_4]\text{Cr}_2\text{O}_7$  separate from the solution. Filter through a filtering crucible, and transfer the precipitate with a solution containing 0.3 g. of ammonium dichromate and 0.3 ml. of pyridine in 100 ml. of water. Then wash 2-3 times with a solution of 0.5-1.0 ml. of pyridine in 100 ml. of acetone, and finally 2-3 times with 2 ml. of ether. The precipitate is then dried 5-10 minutes in a vacuum desiccator and weighed. The factor for copper is 0.1067.

**Separation of copper and antimony.** Vasil'ev and Vorob'eva<sup>30</sup> have used a gravimetric method based upon the formation of the green pyridine thiocyanate complex for the determination of small quantities of copper in metallic antimony of high purity. This determination can be carried out without separating copper from the antimony or other elements which are present. The antimony is kept in solution by addition of tartaric acid.

**Titrimetric determination of copper.** Several titrimetric procedures based upon the precipitation of copper with pyridine and thiocyanate have been proposed. The one which appears to give the best results is based on the precipitation of copper in the presence of pyridine with an excess of a standard solution of potassium thiocyanate, and then titrating the excess thiocyanate with standard silver nitrate solution.<sup>19,20,21</sup>

Curry<sup>22</sup> has proposed titrating the excess of ammonium thiocyanate used in the precipitation with standard potassium permanganate solution, but Golse<sup>21</sup> claims that this titration does not run to completion and consequently does not

give accurate results. The calculation of the permanganate titration is based upon the following equation:



Spacu and Spacu<sup>19</sup> have proposed the following method:

**Procedure.** Place 5 ml. of the solution to be analyzed in a 100-ml. measuring flask, and add 20 ml. of 0.1 N potassium thiocyanate solution and 0.5 ml. of pyridine. Dilute to the mark with distilled water and mix well. Filter, and determine the excess potassium thiocyanate in an aliquot portion of the filtrate by titrating with standard silver nitrate, using a potentiometric method.

This method is suitable for the determination of 0.1-0.001 molar solutions of copper salts.

Tettamanzi<sup>20,157</sup> has used a similar method for determining copper, but has recommended the titration of the excess thiocyanate with silver nitrate using the Volhard method. The results obtained using this method check within 0.25 per cent. Nickel, cobalt, manganese, zinc and cadmium interfere, since they form similar insoluble compounds with pyridine and potassium thiocyanate. The alkali and alkaline earth metals and magnesium do not interfere. This method may be used for the rapid determination of as little as 3 parts of copper in 100,000 parts of solution.

Golse<sup>21</sup> claims that the most accurate determination can be accomplished by precipitating copper with pyridine and an excess of standard thiocyanate; and then, after filtering and acidifying the filtrate with nitric acid, adding an excess of standard silver nitrate and titrating the excess with standard thiocyanate, using ferric alum as the indicator.

**Colorimetric determination of copper.** The green compound formed when a neutral solution of a copper salt is treated with ammonium thiocyanate and pyridine dissolves in chloroform with the formation of an emerald green color. Biazzo,<sup>23</sup> Hester,<sup>24</sup> Elvehjem and Lindow,<sup>25</sup> Schonheimer and Oshima,<sup>26</sup> Oshima and Schonheimer<sup>27</sup> and Benoit<sup>28</sup> have adapted this reaction to the colorimetric determination of very small quantities of copper in organic materials. The following method, described by Biazzo,<sup>23</sup> is rapid and accurate, and requires only small samples:

**Procedure.** Ash 5-10 g. of the sample in an electric furnace at a dull red heat until carbon is completely destroyed. Dissolve the ash in 15 ml. of 1:1 hydrochloric acid and evaporate to dryness on a sand bath. Moisten the residue with 5 ml. of N hydrochloric acid, and then add 5 ml. of water. Warm on a sand bath for 30 minutes, filter, and wash the residue thoroughly to make the total volume of the solution about 100 ml. Evaporate on a hot plate until the volume is about 10 ml. and allow to cool. Transfer the solution to a 25-ml. volumetric flask.

Add N sodium hydroxide until the mixture is just alkaline to phenolphthalein. Add 1 ml. of glacial acetic acid, 1 ml. 10 per cent potassium thiocyanate and 10 drops of pyridine, and then add exactly 5 ml. of chloroform. Dilute to the mark with distilled water. Shake thoroughly and allow to settle. Remove most of the aqueous layer and transfer the remaining water and chloroform to a colorimeter cup. Compare with a standard copper solution similarly prepared. The weight of copper is calculated as follows:

$$\frac{\text{Reading of standard}}{\text{Reading of unknown}} \times \frac{\text{mg. Cu in standard}}{\text{mg. Cu in aliquot}} \times \frac{100}{\text{aliquot}} = \text{mg. Cu per 100 ml. or g.}$$

Schonheimer and Oshima<sup>26</sup> have applied this method to the determination of copper in normal and pathological organs, and have reported that 0.01 mg. of copper can be determined with a maximum error of 5 per cent, and 0.008 mg. of copper with a maximum error of 8 per cent.

Elvehjem and Lindow<sup>25</sup> have used a modification of the method of Biazzo, but report that two important difficulties are encountered in applying this procedure to the determination of small quantities of copper in biological materials: In the presence of a few mg. of ferric iron a brownish color, or with ferrous iron, a greenish color, is formed in the chloroform layer; and the calcium phosphate present in organic materials remains undissolved in the acetic acid and causes the subsequent extraction of the copper compound to be incomplete. To determine copper in the presence of iron, Chalk<sup>29</sup> proposes the following procedure:

**Procedure.** Make 35 ml. of the solution to be analyzed, containing up to 0.1 mg. of copper, slightly alkaline with N sodium hydroxide to phenolphthalein. Add sufficient N sulfuric acid to dissolve the precipitate of ferric hydroxide and form a clear light yellow solution. About 3 ml. of N sulfuric acid is sufficient to dissolve 40 mg. of ferric hydroxide. In those cases where the iron content is not known, avoid an excess of the sulfuric acid by adding 1 ml. at a time, and allowing to stand with occasional shaking for 5 minutes after each addition until the solution is clear and light yellow. Transfer the mixture to a 60 ml. separatory funnel with the stem cut off close to the stop cock, and with a 50 ml. mark etched on the glass. Add 1 ml. of 10 per cent tartaric acid, and immediately add 1 ml. of 10 per cent potassium thiocyanate solution, 0.5 ml. of pyridine and 5 ml. of chloroform. The chloroform must be accurately measured. Dilute to 50 ml., shake for 15 seconds, and run off the chloroform layer into a 25 ml. Nessler tube. Compare the resulting green solution with standards similarly prepared.

All reagents should be tested to be certain that no copper is present. As little as 0.001 mg. of copper can be detected by this procedure. Nickel and cobalt salts give blue and pink precipitates respectively with pyridine and thiocyanate and must be absent in making the determination. Silver and mercurous salts form compounds which are insoluble in chloroform, thereby causing incomplete extraction. Potassium cyanide interferes by preventing the formation of the copper precipitate. Acetates must be absent. In the presence of

lead and barium, hydrochloric acid must be substituted for sulfuric acid in the procedure, since with the latter, lead and barium form insoluble salts.

Kleinman and Klinke<sup>169</sup> report that bromobenzene is somewhat more satisfactory as a solvent for the copper pyridine thiocyanate complex than chloroform. The following procedure illustrates this use.

**Procedure.** To both standard and sample add 1 ml. of glacial acetic acid and 30 drops of pyridine. Add 3 ml. of 10 per cent potassium thiocyanate solution and 2 ml. of bromobenzene, accurately measured. Shake well, and allow the bromobenzene to settle. Draw off the green layer and compare with a standard similarly and simultaneously prepared. The comparison is best carried out by the balancing method in a microcolorimeter. The size of sample or quantity of bromobenzene may be varied to give a color suitable for comparison.

The determination of copper with pyridine and thiocyanate is slightly less sensitive than similar procedures employing diethyldithiocarbamate, but it possesses the advantage that after oxidation, metals other than nickel, cobalt and silver do not interfere.

Lur'e and Ginzburg<sup>31</sup> have used a colorimetric procedure for determining copper in low grade ore and flotation tailings. They found that the method gave equally good results with or without the removal of the insoluble residue. They recommend the formation of the complex in a citric acid and not in a tartaric acid medium.

Less than 0.01 mg. of copper can be separated from solutions containing iron by extracting with chloroform the copper pyridine thiocyanate complex.<sup>167</sup>

Goethals<sup>32</sup> has studied the formation of a blue copper pyridine complex in order to determine its applicability to the colorimetric determination of copper. Copper forms with pyridine in a weakly acid solution a bluish complex compound, but in an alkaline solution copper hydroxide precipitates and this does not redissolve in pyridine. In neutral solutions a turbidity of copper hydroxide results from the small quantities of pyridine. Further, the color of the solution obtained by adding pyridine to copper salts depends upon the concentration of the pyridine. The following procedure is recommended:

**Procedure.** To a weakly acid solution of a copper salt which is not more than 0.01 molar in hydrochloric acid, add 10 ml. of pyridine and dilute with water to 300 ml. Compare the absorption of this solution with that of a standard solution similarly prepared, using an orange-red filter.

**Detection of nickel and cobalt.** When pyridine and ammonium thiocyanate are added to solutions containing cobalt salts, a pink precipitate of  $[\text{CoPy}_4](\text{SCN})_2$  is formed. A blue precipitate is formed when dilute nitric acid is added to an aqueous suspension of this precipitate. The blue precipitate quickly dissolves upon the addition of sufficient nitric acid and a red solution is obtained. From this solution blue needles separate which correspond in composition to  $[\text{CoPy}_2](\text{SCN})_4\text{H}_2\cdot 2\text{Py}$ . This same compound is obtained if,

without isolating the above-mentioned pink salt, the reaction is carried out by mixing cobalt chloride, ammonium thiocyanate and pyridine, and adding nitric acid to the paste so formed until the crystals turn blue. The formation of these crystalline compounds with pyridine and ammonium thiocyanate and with pyridine, ammonium thiocyanate and nitric acid has been used for the micro-detection of cobalt.<sup>3,4,150</sup>

Solutions of nickel salts also react with ammonium thiocyanate and pyridine to yield a crystalline precipitate of  $[\text{NiPy}_4](\text{SCN})_2$ . This can be used for the microdetection of nickel.

Korinskii<sup>2</sup> has used the capillary properties of filter paper to detect cobalt, iron and copper in a solution in which all are present. These ions are detected by the products formed when they react with ammonium thiocyanate and pyridine, and the technique employed depends upon the diffusion of the salts of different metals through a strip of filter paper. Iron occupies the lowest portion of the paper, copper the middle and cobalt the upper portion. In this manner it is possible to detect 10% of cobalt in the presence of 20 times as much iron.

Dobbins and Gilreath<sup>164</sup> have precipitated as a group in a systematic scheme of analysis the metals, copper, zinc, nickel, cobalt and cadmium.

Mercury, copper, cadmium, cobalt, nickel, zinc, manganese, chromium, lead, silver and iron yield with pyridine and potassium dichromate difficultly soluble salts which possess recognizable crystalline forms.<sup>5,6</sup> Korenman<sup>7</sup> has used these reactions for the microchemical identification of these metals. The formulas for the nickel and cobalt salts are  $[\text{NiPy}_4]\text{Cr}_2\text{O}_7$  and  $[\text{CoPy}_4]\text{Cr}_2\text{O}_7$  respectively. The following procedure may be used to detect cobalt and nickel:

**Procedure.** Add a few drops of a saturated solution of potassium dichromate to a drop of the solution to be tested on a glass slide and treat with pyridine vapor. Rub with a glass rod and again treat with pyridine vapor. If the solution is very dilute repeat the rubbing and treatment with pyridine vapor. The crystals of the nickel or cobalt compound can be recognized by examining the mixture under a microscope. By this procedure 0.1% of cobalt and 0.4% of nickel can be detected.

In a recent critical review of the reagents used for the detection of nickel, Wenger, Duckert and Busset<sup>33</sup> recommend the above procedure as one of the most satisfactory for the microdetection of nickel.

**Determination of nickel and cobalt.** *Gravimetric determination of nickel:* Nickel is precipitated quantitatively as  $[\text{NiPy}_4](\text{SCN})_2$  when a neutral solution of a nickel salt is treated with pyridine and an alkali thiocyanate. Spacu<sup>34,35</sup> has used this reaction for the gravimetric determination of nickel. The nickel precipitate may be washed, dried and weighed as such, or ignited and weighed as nickel oxide. In the following procedure, nickel is weighed as nickel oxide:<sup>34</sup>

**Procedure.** Add at room temperature and with constant stirring an excess of a concentrated solution of ammonium thiocyanate and an excess of pyridine to the solution containing the nickel. After the blue precipitate has formed, heat almost to boiling with stirring, and then cool gradually to room

temperature. Decant the supernatant liquid from the precipitate, and wash free from ammonium thiocyanate with the addition of 5 per cent pyridine. Dry in a porcelain crucible at 130° C. and incinerate slowly, and then heat with a blast lamp for two or three hours. The final heating must be carried out in a covered crucible in order to reduce traces of  $\text{Ni}_2\text{O}_3$  to  $\text{NiO}$ .

It is possible to determine thiocyanate by precipitating with nickel and pyridine in a manner similar to that described above.

In the following procedure, nickel is determined by precipitation of  $[\text{NiPy}_4](\text{SCN})_2$  and weighing in this form after washing and drying:<sup>35</sup>

**Procedure.** Add 0.5-1.0 g. ammonium thiocyanate to 100 ml. of a solution containing 0.1-0.2 g. of nickel. Heat to boiling, and then precipitate by the dropwise addition of 1-2 ml. of pyridine. Cool, filter through a filtering crucible, and wash with each of the following wash liquids:

(a) Use to transfer the precipitate to the filtering crucible, a solution prepared by adding 4 g. of ammonium thiocyanate, and 6 ml. of pyridine to 1 liter of water.

(b) Wash twice with 1-ml. portions of a solution composed of 370 ml. of 95 per cent alcohol, 615 ml. of water, 15 ml. of pyridine and 1 g. ammonium thiocyanate.

(c) Wash twice with 1-ml. portions of a 5 per cent solution of pyridine in absolute alcohol.

(d) Wash 5-6 times with ethyl ether containing 2 drops of pyridine in each 20 ml. Then dry in a vacuum at room temperature and weigh. The factor for nickel is 0.1195.

**Gravimetric determination of cobalt.** When a solution of a cobaltous salt is treated with an alkali thiocyanate and an excess of pyridine, the compound  $[\text{CoPy}_4](\text{SCN})_2$  is quantitatively precipitated. By means of this reaction cobalt can be determined quickly and accurately in the presence of the alkaline earths and certain other metals, but copper, cadmium, nickel, manganese and zinc yield similar precipitates. The cobalt complex is slightly soluble in water, ethyl alcohol and ether, but is insoluble in amyl alcohol. The complex is soluble in methyl alcohol and chloroform. It is insoluble in alcohol containing an alkali thiocyanate and pyridine; in ether containing pyridine; and only traces dissolve in absolute alcohol containing pyridine. The following procedure has been used by Spacu and Dick:<sup>36</sup>

**Procedure.** If the solution is neutral, add pyridine until a slight precipitate is formed, and then heat until the precipitate dissolves. If the solution is strongly acid, evaporate to dryness and take up the residue with water. The solution should have a volume of about 80 ml. To this add 0.5 g. of ammonium thiocyanate for each 0.1 g. of cobalt and heat to boiling. Then add 1 ml. of pyridine and remove from the source of heat. If the quantity of cobalt is fairly large, add 1 g. of ammonium thiocyanate in excess and a total of 2-3 ml.



of pyridine. Stir well and when the precipitate is crystallized, filter through a Munroe filter. Transfer the precipitate to the filter with a solution containing 7 ml. of pyridine and 5 g. of ammonium thiocyanate per liter. Wash the precipitate six times with a liquid prepared by mixing 130 ml. of 95 per cent alcohol, 855 ml. of water, 15 ml. of pyridine, and 1 g. of ammonium thiocyanate. Finally wash with 1 ml. of absolute alcohol containing 8 per cent pyridine and 8 times with ethyl ether containing 4 drops of pyridine for each 30 ml. Dry the precipitate for 10 minutes in a vacuum and weigh. The factor for cobalt is 0.12002.

Mukhina<sup>37</sup> has used pyridine and ammonium thiocyanate to determine cobalt in the analysis of special steels. The cobalt, together with nickel, copper and zinc, is precipitated with pyridine and ammonium thiocyanate as  $[\text{CoPy}_4](\text{SCN})_2$ , while ~~iron~~ and chromium are retained in solution with the aid of tartaric acid.

**Procedure.** Dissolve 1 g. of the steel to be analyzed in nitric and sulfuric acids and dilute with water. Evaporate to 75 ml. and neutralize with ammonium hydroxide to a slight acidity and add 6-8 ml. of 50 per cent tartaric acid. Then add 0.5 g. of ammonium thiocyanate and 1 ml. of pyridine for each 0.1 g. of cobalt present. Cool to 15° C., filter, wash the precipitate with water containing 0.5 per cent ammonium thiocyanate and 0.7 per cent pyridine. Ignite and weigh as  $\text{Co}_3\text{O}_4$ .

Nickel is precipitated with the cobalt, and is determined with dimethylglyoxime. Cobalt is then determined by difference. An excess of sulfuric and tartaric acids must be avoided, since otherwise low values are obtained. Chlorides should also be absent, and the volume of the solution should not exceed 75-100 ml. An excess of pyridine dissolves the precipitate. Manganese is precipitated at 15° C., but it dissolves when the temperature is raised to 22° C.

The above method is not suitable for the determination of as little as 0.1-0.5 per cent of cobalt in the presence of considerable quantities of nickel.

**Precipitation of cobalt and nickel sulfides.** Cobalt and nickel are usually precipitated as the sulfides by means of ammonium sulfide from solutions containing calcium, magnesium and the alkalis. This procedure presents several objectionable features which are sources of error and cause a longer time for the completion of the analysis. These are:

(a) Nickel and cobalt sulfides are precipitated in an amorphous state, and, because of the great surface developed, have great adsorbing qualities.

(b) The precipitates are difficult to filter.

(c) Nickel and cobalt sulfides, particularly the former, form colloids which pass through the filter.

(d) When carbonate is contained in the ammonium sulfide, the alkaline earths may be precipitated.

Ostroumov<sup>47,53,54</sup> has found that nickel and cobalt salts yield crystalline sulfides by precipitation with hydrogen sulfide in the presence of pyridine. The crystalline sulfides are easily filtered, do not oxidize in air, and are free from alkaline earth carbonates. The precipitation may be carried out as follows:

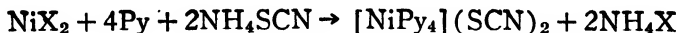
**Procedure.** Treat a neutral or slightly acid solution containing nickel or cobalt chloride with a solution of pyridine chloride (for cobalt or nickel chlorides), or pyridine nitrate (for cobalt and nickel nitrates and sulfates). Dilute with water and heat, and then treat with an excess of 20 per cent pyridine and a stream of hydrogen sulfide for 20 minutes.

This method may be used for the precipitation of nickel and cobalt as a part of the usual scheme of systematic analysis of the cations.<sup>48-52</sup> Pyridine may also be used in the separation of ions of the third analytical group from calcium and magnesium and the alkali metals. The third group metals are precipitated with hydrogen sulfide in the presence of hexamethylenetetramine and pyridine hydrochloride.<sup>158</sup>

**Separation of cobalt and nickel from manganese.** Nickel and cobalt are usually separated from manganese by precipitation as nickel and cobalt sulfides in an acetic acid medium. In general this procedure does not give a good separation. When the solution containing manganese is heated and treated with hydrogen sulfide in the presence of pyridine, a compact, gray-green precipitate of manganese sulfide is formed, and pyridine alone does not prevent the precipitation of the manganese. When pyridine hydrochloride is used along with the free base, manganese is not precipitated at all. Pyridine salts added to solutions containing pyridine lower the pH due to buffer action, and this prevents the precipitation of manganese sulfide. It is also possible that soluble complex compounds of pyridine and manganese salts are formed. The following procedure<sup>54,55</sup> gives a quantitative separation of cobalt and nickel from manganese:

**Procedure.** To 200 ml. of a neutral or slightly acid solution containing cobalt, nickel and manganese, add a mixture of 5 ml. of concentrated hydrochloric acid, 20-25 ml. of water, and sufficient pyridine to make the mixture basic to methyl red. Heat the solution to boiling, add 5-10 ml. of 20 per cent pyridine solution, and saturate with hydrogen sulfide for 10-15 minutes. The precipitate of nickel and cobalt sulfides may be filtered off while manganese remains in solution.

**Titrimetric determination of nickel and cobalt.** Nickel may be determined by a titrimetric procedure based upon the complete precipitation of the nickel from an aqueous solution by means of an excess of 0.1 N potassium or ammonium thiocyanate in the presence of pyridine according to the following reaction



and subsequent titration of the excess thiocyanate with 0.1 N silver nitrate solution.<sup>33,34,37,39,40-44</sup> Nickel is determined by the relationship:  $2\text{SCN}^- = 1 \text{ Ni}$ .

Spacu and Ripan<sup>34</sup> have developed two practical titration procedures:

**Procedure.** Dissolve the sample in 25-30 ml. of water and add 8-10 drops of pyridine. Add a measured excess of standardized 0.1 N ammonium thiocyanate solution, and heat the solution almost to boiling with constant stirring. Allow to cool and filter off the supernatant liquid. Wash the precipitate several times by decantation, using a total volume of 100-150 ml. of 5 per cent aqueous pyridine. Place the filtrate and washings in an Erlenmeyer flask, and make slightly acid with dilute nitric acid. Now add a measured excess of standard 0.1 N silver nitrate solution, and titrate the excess with 0.1 N ammonium thiocyanate, using ferric alum as the indicator. One ml. of 0.1 N ammonium thiocyanate is equivalent to 2.934 mg. of nickel.

The second method is carried out as follows:

**Procedure.** Transfer the weighed sample to a 100-ml. volumetric flask and dissolve in 50-60 ml. of water. Precipitate nickel as described in the above procedure, and dilute the contents of the flask to about 75 ml. Place the flask on a cold water bath and slowly heat to boiling. Shake occasionally during the heating period. Allow to cool, dilute to the mark, mix thoroughly, and filter through a dry filter into a dry flask. Remove an aliquot with a pipet, and titrate as described in the above procedure.

The same method may be applied to the determination of cobalt. The following procedure for the titrimetric determination of cobalt has been proposed by Spacu and Kuras:<sup>38</sup>

**Procedure.** Heat 50-60 ml. of a solution containing 0.02-0.05 g. of cobalt on a water-bath, and add 1 ml. of pyridine and a measured volume of 0.1 N ammonium thiocyanate solution. Filter and titrate the excess thiocyanate with 0.1 N silver nitrate solution, using a nitric acid solution of ferric alum as the indicator.

Spacu and Spacu<sup>33,43</sup> have determined nickel indirectly by a potentiometric method which depends upon precipitating nickel with pyridine and an excess of potassium thiocyanate, and titrating the excess thiocyanate potentiometrically with silver nitrate:

**Procedure.** To 10 ml. of the nickel solution in a 100-ml. measuring flask, add 20 ml. of 0.1 N potassium thiocyanate solution and 0.5 ml. of pyridine. Allow the precipitate to settle, dilute to the mark and mix well. Filter through a dry paper and use 50 ml. of the filtrate. Neutralize to methyl orange with nitric acid, add 30-40 ml. of water and then titrate with 0.1 N silver nitrate solution, determining the end-point potentiometrically.

The results obtained by this method are within 0.5 per cent of the correct value. Cobalt may be determined by a similar method.<sup>44</sup>

Dobbins and Sanders<sup>39</sup> have found the method of Spacu<sup>38</sup> unsatisfactory, since they claim it is impossible to wash out all the excess thiocyanate without

dissolving some of the complex salt. Accordingly they have recommended the following procedure:

**Procedure.** Place the sample, which contains 0.05-0.1 g. of cobalt as the cobaltous salt, in a 250-ml. volumetric flask and dissolve in 150 ml. of water. Make the solution just acid to litmus with nitric acid, add 3 ml. of pyridine, and then run in an excess of a standard 0.1 N ammonium thiocyanate solution. Dilute to the mark and mix thoroughly. Filter a portion of the solution through dry paper and discard the first few ml. of the filtrate. Transfer a 50-ml. aliquot of the filtrate to a beaker and dilute to 100 ml. Add 1 ml. of concentrated nitric acid and immediately run in an excess of standard 0.1 N silver nitrate solution. Add 5 ml. of an indicator prepared by dissolving 10 g. of ferric alum in a mixture of 80 ml. of water and 20 ml. of 6 N nitric acid, and then complete the titration in the usual manner. The error caused by the precipitate in the solution is negligible. The weight of cobalt is calculated from the following equation:

$$\text{g. Co} = (\text{ml. of } 0.1 \text{ N NH}_4\text{SCN}) - 5 (\text{ml. } 0.1 \text{ N AgNO}_3) \times 0.02947$$

The same procedure may be employed for the determination of nickel. The authors claim excellent results for this method.

Spacu and Macarovici<sup>39,40</sup> have determined cobalt and nickel simultaneously by precipitating as  $[\text{CoPy}_4](\text{SCN})_2$  and  $[\text{NiPy}_4](\text{SCN})_2$  with pyridine and ammonium thiocyanate and weighing together; and, after determining nickel with dimethylglyoxime in another portion of the solution, determining the weight of cobalt by difference.

**Procedure.** Place the weighed mixture of nickel and cobalt salts in a volumetric flask and dissolve in a little water. Dilute to the mark and mix well. Dilute a measured volume of this solution with water to 60-80 ml. and add 1-2 ml. of pyridine and heat to boiling. Add 10 ml. of approximately 10 per cent ammonium thiocyanate solution and stir well. The rose colored cobalt salt and the violet nickel salt separate from the solution on cooling. Filter when cold and transfer the precipitate to a filtering crucible with 30 per cent alcohol containing 1 g. of ammonium thiocyanate and 15 ml. of pyridine per liter. Wash the precipitate twice with an 8 per cent solution of pyridine in absolute alcohol and drain well after each washing. Finally, wash 5-6 times with ether containing 1 per cent pyridine, and dry in a vacuum desiccator and weigh. In another portion of the solution determine nickel with dimethylglyoxime in the usual manner, and determine the cobalt by difference.

This determination can be carried out in the presence of iron if Rochelle salt is added to prevent precipitation of ferric hydroxide, or if the iron is first removed by precipitation with pyridine (page 16).

Cobalt and nickel can be determined simultaneously by means of a polarographic method.<sup>45</sup> The half-wave potentials of nickel and cobalt differ only by 0.1 v. in a 1 N potassium chloride solution, but they are separated by 0.29 v.

in 1 N potassium chloride + 0.5 M pyridine. If the supporting electrolyte contains equal concentrations of pyridine and a pyridinium salt and 0.01 per cent gelatin to suppress the maxima, the nickel and cobalt waves are well separated and easily measurable for a simultaneous determination. The pH of this solution is about 5.4 so that any iron is precipitated. Chromium, which is not precipitated alone at this pH, is co-precipitated with iron if iron is present in excess. Small amounts of copper and manganese do not interfere with this procedure. Small quantities of nickel in  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  are determined with an estimated accuracy of  $\pm 3$  per cent.

Spacu and Armeanu <sup>42</sup> have developed a titrimetric method for determining nickel which resembles in principle the potassium cyanide titration method of Moore, except that the potassium cyanide solution used in the titration contains pyridine. On the addition of this reagent to a nickel solution a light violet precipitate is formed according to the following equation,



and this precipitate dissolves in an excess of potassium cyanide to form  $[\text{Ni}(\text{CN})_4]^-$ . Nickel can be determined by a direct or indirect procedure based upon these reactions. The direct procedure is carried out as follows:

**Reagents.** *Potassium cyanide solution:* Dissolve 20 g. of potassium cyanide and 10 ml. of pyridine in enough water to make a liter of solution and standardize against a pure nickel solution the day it is to be used.

*Nickel nitrate solution:* Prepare a 0.1 N solution of nickel nitrate. The solution need not be exactly 0.1 N but the titer of the solution must be accurately determined.

**Procedure.** Add 1 ml. of pyridine to a measured volume of the potassium cyanide solution, and titrate with the neutral nickel solution to be analyzed until the light violet precipitate begins to dissolve slowly. Then add 100 ml. of hot water and heat the mixture until the solution becomes clear. Again add the nickel solution dropwise until finally a slight precipitate is formed which does not dissolve within 2 or 3 minutes.

An alternate method is to titrate the unknown nickel solution dropwise with the potassium cyanide solution until the solution becomes clear after 2 or 3 minutes. The potassium cyanide solution must be standardized in exactly the same way that it is used in the procedure.

Nickel may be determined indirectly by the following method:

**Procedure.** Add a few drops of pyridine to a solid nickel salt or a concentrated neutral solution of the salt, and titrate in the cold with continuous stirring until an excess of the standard potassium cyanide solution has been added. This is indicated by the fact that the light violet precipitate is completely dissolved and the resulting solution is pale yellow in color. Now back

titrate with the standard nickel solution until a permanent turbidity appears in the stirred solution, and which does not dissolve after 2 or 3 minutes.

Nicolaysen <sup>46</sup> has determined cobalt by first precipitating as the cobalt tetrapyridine thiocyanate, and then titrating the cobalt compound with potassium iodate.

**Precipitation of iron, aluminum, chromium, uranium, titanium and zirconium.** *Separation of iron, aluminum and chromium from manganese, cobalt and nickel:* A number of separations have been based upon the fact that iron, aluminum, chromium, uranium, zirconium and titanium are quantitatively precipitated by the addition of an excess pyridine to solutions containing these ions.<sup>56-58</sup>

These reactions have been extensively studied by Ostroumov,<sup>56-59</sup> who recommends the following procedure for separating iron, aluminum and chromium from manganese, cobalt and nickel:

**Procedure.** The precipitation of 20 mg. of iron, aluminum or chromium is made quantitative by adding a 20 per cent pyridine solution to the hot solution containing the cation until the color of the solution is yellow to methyl orange and then adding an additional 10-15 ml.

A good separation of the tri- and bivalent ions occurs with a single precipitation when 20 mg. of the three trivalent metals and a similar quantity of cobalt, nickel and manganese are present in the same solution. The separation is more effectively carried out in the presence of an ammonium salt, which causes the precipitate to settle more quickly.

In the quantitative precipitation of zirconium and titanium with an excess of pyridine, highly dispersed basic salts are formed by hydrolysis, and this may result in considerable loss during filtration. The formation of these basic salts is eliminated in the analysis of 0.1 g. of the ion in 100 ml. of solution by the addition of 5-10 g. of ammonium chloride. If any considerable quantity of precipitate is formed, it should be washed with a 2 per cent solution of ammonium nitrate or chloride containing a little pyridine. The separation is not satisfactory in the presence of zinc ions, since some zinc may also precipitate along with iron, chromium and aluminum. If nickel is to be determined in the filtrate with dimethylglyoxime, the excess pyridine must be removed by boiling with a sodium carbonate solution, since pyridine interferes with the nickel determination.

Mendez and Pinto <sup>61</sup> have made a study of the comparative values of pyridine and ammonia for precipitating the hydroxides of iron, aluminum and chromium from solutions containing nickel, cobalt and manganese. They have shown that while a more complete precipitation is obtained with the use of ammonia, precipitation with pyridine in the absence of zinc and sulfate is quantitative if a concentrated pyridine solution is added slowly to the mixture, and the resulting

precipitate filtered after standing in the cold for 24 hours. The precipitate obtained by the use of ammonia, however, contains small quantities of nickel, cobalt and manganese, while pure precipitates are obtained when pyridine is used as the precipitant.

Macarovici<sup>62</sup> has studied the separation of iron, aluminum and chromium from cobalt, nickel and manganese and reports that the procedure employing pyridine is not entirely satisfactory. According to the results of forty-five experiments, Macarovici claims that there is some difficulty in obtaining a complete precipitation of aluminum and chromium by means of pyridine, and that the precipitates so obtained also contain appreciable quantities of nickel, cobalt and manganese. The error is particularly serious in the presence of nickel but least so in the presence of manganese.

**Separation of iron from copper and nickel.** When a solution containing ferric and cupric ions is treated with a slight excess of pyridine, iron is precipitated as ferric hydroxide and copper remains in solution as a complexation. This reaction affords a convenient method for separating iron and copper.<sup>63</sup> Ferric hydroxide may be recovered by filtration and converted into ferric oxide by ignition. Copper is conveniently determined in the filtrate by the addition of ammonium thiocyanate, which, in the presence of an excess of pyridine, precipitates copper as insoluble  $[\text{CuPy}_4](\text{SCN})_2$ . This precipitate can be filtered and weighed as such, or converted to cupric oxide by ignition. A similar procedure may be employed for separating iron and nickel. Nickel, like copper, is converted into insoluble  $[\text{NiPy}_4](\text{SCN})_2$ , and determined in the usual manner.

In the following procedure, which is recommended by Spacu and Niculescu,<sup>64</sup> copper is precipitated with potassium dichromate in the presence of pyridine.

**Procedure.** Add nitric acid to 40-50 ml. of a solution containing iron and copper and heat, if necessary, to oxidize the ferrous to ferric iron. Add a little ammonium chloride and precipitate iron by the addition of a slight excess of pyridine. Filter, dissolve the precipitate in hot 6 N hydrochloric acid, nearly neutralize with ammonium hydroxide and reprecipitate with pyridine. Wash, ignite and weigh as  $\text{Fe}_2\text{O}_3$ . To the combined filtrates, whose volume should not exceed 120 ml., add 1 ml. of pyridine and heat to 30-40° C., and then precipitate  $[\text{CuPy}_4]\text{Cr}_2\text{O}_7$  by the addition of a concentrated solution of potassium dichromate. Filter, wash the precipitate with a 0.3 per cent potassium dichromate solution containing 3 ml. of pyridine per liter, then with acetone containing 1 drop of pyridine, and finally with ether. Dry in a vacuum desiccator and weigh. The factor for copper is 0.1067.

**Separation of iron and cobalt.** Spacu<sup>60</sup> recommends the following procedure for the separation of iron and cobalt:

**Procedure.** Add pyridine dropwise to 50-80 ml. of a hot solution containing ferric and cobaltous ions until the iron is completely precipitated as ferric hydroxide, and then add a few drops in excess. Filter, wash, ignite and

weigh as  $\text{Fe}_2\text{O}_3$ . A second precipitation is advisable to remove any cobalt that may have been carried down by the ferric hydroxide precipitate.

**Separation of iron from manganese.** No precipitate is formed when pyridine is added to a neutral solution of a manganese salt, and even on boiling the oxidation of manganese proceeds only about one-third as rapidly as when treated with ammonium chloride and ammonium hydroxide under similar conditions. If a solution containing manganous ions is acidified with a little hydrochloric acid and then treated with a slight excess of pyridine, the solution can be heated for 10 minutes without oxidation of the manganese. Under similar conditions ferric iron is entirely precipitated as ferric hydroxide, which can be washed with a 0.2 per cent aqueous solution of pyridine without loss. In this way iron and manganese can be separated satisfactorily.<sup>64,66-68</sup>

**Procedure.** Add nitric acid to 40-50 ml. of a solution containing iron and manganese, and heat, if necessary, to convert the ferrous to ferric iron. Add a little ammonium nitrate and precipitate iron as ferric hydroxide with a slight excess of pyridine. Filter, dissolve the precipitate in hot 6 N hydrochloric acid, neutralize with ammonium hydroxide, and again precipitate with pyridine. Wash, ignite and weigh as  $\text{Fe}_2\text{O}_3$ .

Manganese can be determined in the filtrate by precipitation as manganous ammonium phosphate by method of Dick.<sup>65</sup>

**Separation of iron and mercury.** When ammonium thiocyanate and an excess of pyridine is added to a solution containing a mercuric salt, a soluble complex mercury ion,  $[\text{HgCl}_2(\text{CNS})_2]$ , is formed; but with similar treatment ferric iron is completely precipitated as ferric hydroxide. This difference in the behavior of mercuric and ferric salts makes possible a satisfactory separation of these cations.<sup>69-71</sup>

**Procedure.** To 100-150 ml. of a dilute solution containing about 0.2 g. of mercury and 0.1 g. of iron as mercuric and ferric salts, add 3-4 times as much solid potassium thiocyanate as the combined weight of the iron and the mercury in the solution. Now add pyridine drop by drop to the dark red solution until the color changes to a reddish-brown. Then add 3-4 drops of pyridine in excess and heat to boiling. Filter off the precipitated ferric hydroxide, wash with hot water, and ignite and weigh as  $\text{Fe}_2\text{O}_3$ .

Mercury is determined in the filtrate by acidifying with hydrochloric acid and precipitating as mercuric sulfide. It is weighed in this form.

**Detection of Lead.** When potassium iodide and pyridine are added to a solution containing a lead salt, a precipitate of  $[\text{PbPy}_2]\text{I}_2$  is formed when as little as 0.25% of lead is present. This compound is white in daylight, but shows a strong yellow-brown fluorescence under ultra-violet light.<sup>72</sup> The formation of this compound may be used for the microdetection of lead.<sup>73</sup>

Lead may be detected by use of a 2 per cent solution of dithizone in pyridine. The test is best made in dilute nitric acid solution of pH 0.5-1.0. The microcrystals may be distinguished even in the presence of mercury and silver.<sup>168</sup>



Pavelka <sup>74</sup> has used gallocyanine in the presence of pyridine in a spot test for lead.

**Procedure.** Place 1 drop of the solution to be tested on a strip of filter paper and add a drop of a dilute pyridine solution. Add a drop of 0.1 per cent solution of gallocyanine, and wash the spot so formed with successive drops of 1 per cent pyridine. A violet stain is formed if lead is present.

The lead may first be precipitated on the paper as lead sulfate before applying the test, and this makes possible the detection of lead in the presence of silver, copper, cadmium and bismuth.

**Determination of lead.** A precipitate of  $\text{Pb(OH)SCN}$  is formed when ammonium thiocyanate is added to a solution of a lead salt that has been neutralized with pyridine. This compound is insoluble in 95 per cent alcohol, in ether, and in water containing pyridine and an alkali thiocyanate. This precipitate can be dried at  $40^\circ\text{C}$ ., or in a vacuum desiccator at room temperature, and weighed in this form.<sup>75</sup>

**Procedure.** The volume of the solution used for the analysis should not exceed 50 ml., and must not contain more than 0.75 g. of lead. To this solution add a concentrated solution of 2 g. of ammonium thiocyanate and 1 ml. of pyridine for each 0.2 g. of lead and stir well. Filter through a Gooch crucible, and wash the precipitate with an aqueous solution containing 2 per cent ammonium thiocyanate and 1 per cent pyridine, then 4-5 times with alcohol, and finally 4-5 times with ether. Suck as dry as possible, and dry 5-6 minutes in a vacuum desiccator at room temperature or for 15 minutes in an oven at  $40^\circ\text{C}$ . Weigh as  $\text{Pb(OH)SCN}$ . The factor for lead is 0.7340.

Ammonium salts tend to dissolve the precipitate of the lead compound and should be absent during the precipitation. For this reason, too, not more than the equivalent of 0.4 g. of lead should be used for the analysis of water-insoluble salts. If the solution to be analyzed is acid, evaporate to dryness several times with nitric acid and then dissolve the residue in water before proceeding with the analysis.

**Separation of lead from other cations.** Lead can be separated from silver, mercury, copper, cobalt, nickel, cadmium, thallium, magnesium, calcium, strontium and barium by precipitating as lead carbonate from solutions containing pyridine by means of carbon dioxide gas. The following procedure is used for the separation of lead from silver:<sup>76</sup>

**Procedure.** To a neutral solution containing not more than 0.2 g. of lead or 0.2 g. of silver, add a 10 per cent aqueous solution of pyridine until the mixture is alkaline to methyl orange. Allow to stand for 5 minutes and add 5 ml. of 98 per cent alcohol and 15 ml. of 10 per cent pyridine solution, and then pass a stream of carbon dioxide gas through the mixture for 45 minutes. Filter and wash the precipitate with 100 ml. of water which has been saturated with carbon dioxide and which contains 4 ml. of alcohol and 4 ml.

of diluted pyridine. Dry at 100° C. and weigh as lead carbonate. Silver remains in solution and is contained in the filtrate.

The following method is used for the separation of lead from mercury:<sup>77</sup>

**Procedure.** Acidify a solution containing about 0.2 g. of lead and 0.2 g. of mercury with a little nitric acid and add pyridine until the solution is neutral to phenolphthalein. Dilute with water to 100 ml. Pass a stream of carbon dioxide gas, which has been washed with a silver nitrate solution, through the mixture for 45 minutes. Allow to stand for 2-3 hours. Filter off the precipitated lead carbonate through a Gooch crucible using suction. The filtration should be carried out at such rate that about 45 minutes are required. Wash the precipitate with a mixture of 92 ml. of water, 4 ml. of 10 per cent pyridine, and 4 ml. of 96 per cent alcohol which has been saturated with carbon dioxide. Dry the precipitate at 120° C. and ignite to constant weight.

Lead can also be separated from solutions containing cobalt, copper, nickel and cadmium. The following procedure is used:<sup>78</sup>

**Procedure.** The solution to be analyzed should contain not more than 0.2 g. of lead, cobalt, copper, nickel and cadmium as the nitrates, and should contain an alkali nitrate. Neutralize the solution, and treat with a 10 per cent solution of pyridine until the mixture is azure-blue in color. Then add an additional 15 ml. of 10 per cent pyridine solution. Dilute with water to 100 ml. and introduce a stream of carbon dioxide (which has been washed in a solution of silver nitrate) to precipitate lead. This requires about 5 minutes. Add 2 ml. of ammonium hydroxide to prevent the precipitation of copper, and then continue the addition of carbon dioxide for 45 minutes. Allow to stand for 1 hour, filter through a Gooch crucible, and wash with a mixture containing 90 ml. of water, 4 ml. of 96 per cent ethyl alcohol, 4 ml. 10 per cent pyridine and 2 ml. of concentrated ammonium hydroxide and saturated with carbon dioxide for 45 minutes. Lead carbonate may be dried at 120° C. to constant weight or ignited to PbO in a protected porcelain crucible in a Bunsen flame.

The separation of lead and copper by this procedure is complete. In the presence of cobalt or nickel, the lead determinations are accurate, but results for cobalt and nickel are usually somewhat lower than the theoretical value. With as much as 0.2 g. of cadmium in 100 ml. of solution, it is necessary to add 16 g. of ammonium nitrate and 0.5 g. of ammonium acetate in order to effect a complete separation of the lead and cadmium. In the presence of equivalent quantities of lead and cadmium, the lead precipitate is contaminated by cadmium. The best separation occurs when there is less cadmium than lead. The separation of lead from copper, cobalt and nickel is complete even in the presence of 2 g. of ammonium carbonate, 3 g. of potassium carbonate, or 4 g. of sodium carbonate per 100 ml. of solution.

A procedure similar to the above is used for separating lead from magnesium, calcium, strontium, barium and thallium.<sup>79</sup>

**Procedure.** To a neutral solution of lead nitrate, containing a maximum of 0.2 g. of lead and 0.2 g. of magnesium, thallium or calcium, add 10 ml. of a 2 N ammonium nitrate solution, 3 ml. of 96 per cent ethyl alcohol and 15 ml. of 10 per cent pyridine solution. Dilute to 100 ml. and pass carbon dioxide through the solution for 45 minutes. Allow the precipitate of lead carbonate to settle and filter through a Gooch crucible. Wash with a mixture of 4 ml. of 96 per cent alcohol, 4 ml. of 10 per cent pyridine solution, and 92 ml. of water that has been saturated with carbon dioxide for 45 minutes. The precipitate may be dried at 110-120° C. and weighed as lead carbonate, or ignited in a protected crucible at 500° C. to PbO.

**Detection and determination of mercury.** Mercury salts react with potassium dichromate and pyridine to form an orange colored, difficultly soluble salt, which possesses a recognizable crystalline form.<sup>5-7,151</sup> This reaction has been used by Korenman<sup>7</sup> for the microdetection of mercury.

**Procedure.** Add a drop of a cold saturated solution of potassium dichromate to a drop of the solution to be tested, and then expose the mixture to the vapor of pyridine. Examine the mixture under a microscope. Both mercurous and mercuric compounds yield precipitates. By means of this reaction as little as 0.075γ of mercury can be detected.

Mercury may be detected by means of a 2 per cent solution of dithizone in pyridine. The test is best carried out in dilute nitric acid solution of pH 0.5-1.0. The microcrystals are detectable even in the presence of silver and lead.<sup>168</sup> When pyridine is added to a solution of a mercuric salt containing ammonium dichromate, a fine orange-yellow precipitate of a complex salt of mercury forms. The formula for the mercury compound is  $[\text{HgPy}_2]\text{Cr}_2\text{O}_7$ .<sup>5-7</sup> This compound is insoluble in water containing dichromate and pyridine, and in alcohol and in ether. This reaction has been used by Spacu and Dick<sup>80</sup> for the gravimetric determination of mercury.

**Procedure.** Add 2 g. of powdered ammonium dichromate to 100 ml. of the solution containing not more than 0.3 g. of the mercuric salt, and as soon as the dichromate has dissolved, add 1 ml. of pyridine. Stir for 5-10 minutes and filter through a Gooch crucible. Wash the precipitate 4-5 times with a solution prepared by dissolving 0.5 g. of ammonium dichromate and 0.5 ml. of pyridine in 1 liter of water, and then wash with 80 per cent alcohol containing 1 drop of pyridine for each 10 ml. of absolute alcohol used in preparing the 80 per cent solution. Finally wash with ether and dry in air or in a vacuum at room temperature and weigh. The factor for mercury is 0.3490.

Furman and State<sup>81</sup> have investigated the procedure of Spacu and Dick and recommend the substitution of methyl acetate for the complicated wash liquids used in the above procedure. They claim that this both simplifies and improves the method. The final determination may be made by dissolving the precipitate in acid and titrating the dichromate either iodometrically or with a ferrous sulfate solution. The results obtained using the titrimetric procedure are reported to be as accurate as those obtained gravimetrically. Ryazanov and Pysheva<sup>82</sup>

have studied various methods for determining mercury and report excellent results may be obtained by precipitating the mercury and weighing as  $[\text{HgPy}_2]\text{Cr}_2\text{O}_7$ .

Aqueous solutions of mercuric chloride form with pyridine a white crystalline precipitate of  $\text{HgCl}_2 \cdot \text{Py}$ , in which Py represents one mole of pyridine. Precipitation is quantitative, but the compound is soluble in an excess of the precipitant. This reaction was first observed by Lang,<sup>83</sup> and has since been used by Rotter<sup>149</sup> for the determination of mercury.

**Detection of zinc.** A white precipitate of  $[\text{ZnPy}_2](\text{SCN})_2$  is formed when a slight excess of ammonium thiocyanate is added to a neutral solution of a zinc salt and the mixture is then treated with a few drops of pyridine. This reaction may be used as a sensitive test for zinc.<sup>4,84-85</sup> A large excess of pyridine must be avoided since the zinc compound dissolves in an excess of the reagent. By means of this reaction as little as one part of zinc in 200,000 parts of water may be detected. This test is limited in value since many of the common cations also form precipitates with pyridine and ammonium thiocyanate.

Solutions of zinc salts react with pyridine and potassium dichromate to yield a difficultly soluble orange salt, which possesses a recognizable crystalline form.<sup>5,6</sup> Korenman<sup>7</sup> has used this reaction for the microchemical identification of zinc.

**Procedure.** Add a few drops of potassium dichromate solution to a drop of the solution to be tested and treat the mixture with pyridine vapor. Rub with a glass stirring rod and again treat with pyridine vapor. If the solution is very dilute this operation should be repeated. Observe the mixture under a microscope for the appearance of characteristic zinc crystals.

A somewhat more satisfactory test for zinc is based upon the formation of either  $[\text{ZnPy}_2]\text{I}_2$  or  $[\text{ZnPy}_2]\text{Br}_2$  by adding an alkali halide and an excess of pyridine to a solution containing the zinc salt. The reaction with bromide is more sensitive than that with either chloride or iodide. This reaction possesses the advantage over the pyridine-thiocyanate reaction in that it is more specific and yields insoluble compounds with fewer cations.<sup>86</sup> Both the iodide and bromide precipitates are very insoluble, and their formation is sufficient to detect 0.01 mg. of zinc at a concentration of 5 mg. per 100 ml. of solution.<sup>87,88</sup>

**Procedure.** Add an excess of pyridine and a little 15 per cent potassium iodide or 10 per cent bromide solution to the liquid to be tested. A precipitate of  $[\text{ZnPy}_2]\text{I}_2$  or  $[\text{ZnPy}_2]\text{Br}_2$  forms if zinc is present.

Cobalt, manganese and nickel are not precipitated by this treatment. Cadmium, however, forms insoluble compounds similar to those with zinc, but the reaction can be used for the detection of either zinc or cadmium, since the zinc compound can be distinguished from the cadmium compound by its behavior in parallel polarized light.<sup>89</sup> The formation of  $[\text{ZnPy}_2]\text{I}_2$  has been used by Ripan<sup>90</sup> for detecting zinc after it is separated from other cations in the usual scheme of analysis.

In a recent survey of the various methods which have been proposed for detecting zinc, Wenger, Duckert and Rieth<sup>91</sup> recommend reactions with pyridine and potassium bromide, potassium iodide, and potassium or ammonium thiocyanates as being among the most useful. By means of micromethods, these investigators claim that 0.1 $\gamma$  of zinc at a dilution of 1:100,000 can be detected. They also report that the test on a macro-scale is satisfactory. They suggest as a disadvantage, however, that nickel may give a similar test.

Dobbins and Gilreath<sup>184</sup> have precipitated as a group in a systematic scheme of analysis the metals, copper, zinc, nickel, cobalt and cadmium as the pyridine thiocyanate complexes.

**Determination of zinc.** *Gravimetric determination of zinc:* When a solution containing a zinc salt is treated with an alkali thiocyanate and pyridine, zinc is precipitated quantitatively as  $[\text{ZnPy}_2](\text{SCN})_2$ . The precipitate is a finely crystalline compound when formed in the cold, and may, after filtering and washing, be dried and weighed. This constitutes a satisfactory method for determining zinc.<sup>92-95</sup>

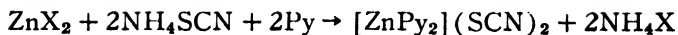
**Procedure.** To a solution containing approximately 0.3 g. of zinc, add water until the total volume is 500 ml. and then add a solution containing 4 g. of ammonium thiocyanate and 2 g. of pyridine in a little water. Allow to stand for about 15 minutes and filter through a Gooch crucible. Transfer the residue to the crucible with a solution prepared by dissolving 3 g. of ammonium thiocyanate and 5 ml. of pyridine in a liter of water. Wash several times with a mixture of 13 ml. of 95 per cent alcohol, 85 ml. of water, 1.5 ml. of pyridine and 0.1 g. of ammonium thiocyanate, and then with a mixture of 10 ml. of alcohol and 1 ml. of pyridine, and finally with 15 ml. of ether containing 2 drops of pyridine. Dry for 10 minutes to constant weight at 65-70° C. and weigh as  $[\text{ZnPy}_2](\text{SCN})_2$ . The factor for zinc is 0.1925.

According to Spacu<sup>84</sup> the complex cannot be weighed, but must be ignited to the oxide.

A negative error of approximately 0.5 per cent occurs when large quantities of ammonium salts are present. Weakly acid solutions are treated with ammonium thiocyanate and neutralized with pyridine, and then treated with an extra ml. of pyridine for the precipitation. Strongly acid solutions are evaporated to dryness and the residue is dissolved in water for the zinc determination. This method provides an excellent means for separating zinc from magnesium and the alkaline earths and the alkali metals.

Spacu and Ripan<sup>96</sup> have adapted the above method to the microchemical determinations of zinc. The zinc pyridine thiocyanate compound is formed in the usual manner, and is then dissolved by repeated extractions of small quantities of chloroform. The residue is weighed after evaporating the chloroform solution to dryness.

**Titrimetric determination of zinc.** Zinc may be determined titrimetrically by means of a method proposed by Spacu and Macarovici.<sup>97</sup> This determination is based on the reaction,



which is usually employed for the gravimetric determination of zinc. In this procedure, however, zinc is precipitated by means of an excess of standardized ammonium thiocyanate solution, and the excess is then titrated with a standard solution of silver nitrate by the method of Volhard, using ferric alum as the indicator.

**Procedure.** Dissolve a weighed quantity of the material to be analyzed in several ml. of water, and transfer the mixture to a 50- or 100-ml. graduated flask. Then add a known excess of a standardized, approximately 0.1 N ammonium thiocyanate solution and 0.5-1.0 ml. of pyridine. Shake the mixture and dilute to the mark with distilled water. Allow to stand for 15 minutes and filter through a dry filter paper into a dry buret. Discard the first 10 ml. of the solution and then measure a suitable volume of the filtered solution into an Erlenmeyer flask and make just acid with nitric acid. Titrate the excess thiocyanate with a standardized 0.1 N solution of silver nitrate by the method of Volhard, using a solution of ferric alum that has been acidified with nitric acid as the indicator. One ml. of 0.1 N  $\text{NH}_4\text{SCN}$  = 0.003269 g. of zinc.

Pagel and Ames<sup>98</sup> have determined zinc iodometrically after precipitation with ammonium thiocyanate and pyridine. In a slightly alkaline solution, iodine reacts with the thiocyanate ion according to the following equation:



When the mixture is acidified, cyanogen iodide reacts instantly and quantitatively with the iodide to form free iodine and the cyanide ion, giving the final quantitative relationship:



The following procedure may be used for the determination of from 3 to 33 mg. of zinc in 100 ml. of solution:

**Procedure.** To the solution of the zinc salt, add 1 g. of solid potassium thiocyanate and 1 ml. of pyridine dropwise with constant stirring. Keep the temperature below 20° C. during the addition of the pyridine. Allow to stand for one hour and filter the crystalline precipitate of  $[\text{ZnPy}_2](\text{SCN})_2$  through a 25 ml. Gooch filter which has been fitted with a disc of filter paper having the edges slightly upturned to fit tightly against the crucible. Wet the filter paper with a solution prepared by dissolving 10 g. of potassium thiocyanate and 10 ml. of pyridine in a liter of water, and then transfer the precipitate to the crucible with this solution. Wash with 10 ml. of anhydrous ether containing 1 per cent of pyridine by volume which has been cooled to a temperature of 20° C. or lower. Transfer the precipitate to a 500-ml. Erlenmeyer flask with the aid of boiling water, and then dilute to 150 ml. with water.

Heat until the precipitate has dissolved, ignoring any small amount of flocculent zinc hydroxide which may form, and add 6 g. of borax and boil for

10 minutes. Cool somewhat, stopper with a clean rubber stopper which has previously been cleaned by boiling with dilute alkali, and then thoroughly cool the mixture with running water. Accurately measure 50 ml. of 0.1 N potassium iodate solution in a second 500-ml. flask, and add 2 g. of potassium iodide and 10 ml. of 1 N hydrochloric acid. Transfer the cooled borax reaction mixture immediately to the second flask containing the potassium iodate and potassium iodide. Wash down the sides of the flask, stopper well, and allow to stand for 10-15 minutes to insure complete oxidation. Then add 10 ml. of 6 N hydrochloric acid and immediately and slowly titrate the excess iodine with 0.1 N sodium thiosulfate until the solution is almost colorless, and then add a little starch indicator and complete the titration. One ml. 0.1 N iodine is equivalent to 0.5446 mg. of zinc.

This method gives excellent results if all details are carefully followed. Chlorides interfere seriously, although nitrates and sulfates seem to be without appreciable effect. Low results are obtained in the presence of ammonium salts,<sup>93</sup> but magnesium and alkaline earths do not interfere. Table 1 shows the results obtained with this method using pure zinc sulfate solution for the analysis:

TABLE 1.—RESULTS OBTAINED USING PURE ZINC SULFATE SOLUTIONS

Zn Used mg.	Zn Found mg.	Error Per Cent
17.98	17.93	—0.3
17.98	17.94	—0.2
17.98	17.98	0.0
17.98	18.03	+0.3
8.21	8.23	+0.2
8.21	8.17	—0.5
3.286	3.241	—1.4
3.286	3.252	—1.0
3.286	3.247	—1.2

**Detection of cadmium.** Cadmium, like zinc, is precipitated from solutions of its salts by the addition of a thiocyanate and pyridine. The formula for the insoluble compound is  $[\text{CdPy}_2](\text{SCN})_2$ . This reaction has been used by Spacu,<sup>99</sup> Martini,<sup>4</sup> and Kolthoff and Hamer<sup>85</sup> for the detection of cadmium. By means of this test cadmium can be detected at a concentration of 0.02 g. per liter. By means of a microtest, as little as 0.05 $\gamma$  of cadmium can be detected by means of the characteristic white crystals which form.

The complex halides of cadmium are precipitated on the addition of pyridine and a soluble halide to a solution of the cadmium salt. The reaction is more sensitive with bromide than with chloride or iodide. A solution of 10 mg. of cadmium in 5 ml. of water is precipitated by the addition of 1-2 g. of sodium bromide and 1 ml. of 10 per cent pyridine. Zinc is also precipitated, but the corresponding halides of pyridine and lead, mercury, copper, nickel, cobalt,

manganese, iron and aluminum are not similarly precipitated. Hence, the pyridine-potassium bromide reaction is much more selective than that with pyridine and thiocyanate, since most of the above metals are precipitated by the latter reagents.<sup>85,86</sup> Although both zinc and cadmium form insoluble compounds with potassium bromide or potassium iodide and pyridine, this reaction can be used for the detection of either zinc or cadmium, since the zinc compound can be distinguished from the cadmium compound by its behavior in parallel polarized light.

The following microchemical test may be used for the identification of as little as 0.5% of cadmium.<sup>89</sup>

**Procedure.** Place a drop of the neutral solution to be tested on a microscope slide, and add a drop of a mixture of equal parts of a 10 per cent potassium iodide solution and pyridine. Examine the resulting precipitate under a microscope.

Pyridine and potassium iodide react with as little as 0.5% of cadmium to form a precipitate of  $[\text{CdPy}_2]\text{I}_2$ , which shows a bluish-white fluorescence in ultra-violet light. Lead also gives a precipitate under the conditions of the test. This precipitate shows a yellowish-brown fluorescence, and consequently interferes with the cadmium test.<sup>72</sup>

Cadmium can also be detected microscopically by means of the insoluble crystalline compound which is formed when potassium dichromate and pyridine are added to a solution containing a cadmium salt.<sup>5,6</sup> Mercury, copper, cobalt, nickel, zinc, manganese, lead, silver and iron also yield precipitates under the conditions of the test and consequently interfere.

Dobbins and Gilreath<sup>184</sup> have precipitated as a group in a systematic scheme of analysis the metals, copper, zinc, nickel, cobalt and cadmium as the pyridine thiocyanate complexes.

**Determination of cadmium.** *Gravimetric determination of cadmium:* If a cold solution containing cadmium and thiocyanate ions is treated with pyridine, a finely crystalline, white precipitate of  $[\text{CdPy}_4](\text{SCN})_2$  is obtained, which is not very stable in air. When the precipitation is carried out at the boiling point, a much more stable precipitate is formed, and this can be washed, dried and weighed for the determination of cadmium. The composition of this precipitate is  $[\text{CdPy}_2](\text{SCN})_2$ .<sup>82,100,101,155</sup> This complex salt is insoluble in water containing pyridine and an alkali thiocyanate. It is also insoluble in ether containing pyridine.

**Procedure.** To 50-100 ml. of the solution to be analyzed, which should contain no ammonium chloride or ammonium acetate, add 0.5-1.0 per cent of solid ammonium thiocyanate and heat to boiling. Add 1 ml. of pyridine and stir well. Allow to cool and filter into a filtering crucible. Wash four times with a solution prepared by mixing 73 ml. of water, 25 ml. of 95 per cent alcohol, 2 ml. of pyridine, and 0.1 g. of ammonium thiocyanate. Then wash once or twice with a 10 per cent solution of pyridine in absolute ethyl alcohol, and finally with 15 ml. of ether containing 2 drops of pyridine. Dry the washed precipitate in a vacuum



desiccator for 10 minutes and weigh as  $[\text{CdPy}_2](\text{SCN})_2$ . The factor for cadmium is 0.2907.

Results obtained by this method are excellent except in the presence of large amounts of ammonium chloride or small amounts of ammonium acetate. It is very important that the cadmium should not precipitate immediately on adding the pyridine (caused by too concentrated a solution), and that the solution should be very hot, since otherwise some  $[\text{CdPy}_4](\text{SCN})_2$  may be formed. This compound is gradually converted to  $[\text{CdPy}_2](\text{SCN})_2$  by long drying in a vacuum desiccator.

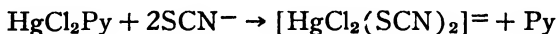
Vornweg<sup>102</sup> has based a method for the determination of cadmium on the formation of  $[\text{CdPy}_4](\text{SCN})_2$ .

**Procedure.** To a neutral solution containing the cadmium salt, add 1 g. of ammonium thiocyanate and precipitate cadmium as  $[\text{CdPy}_4](\text{SCN})_2$  by adding 10-15 ml. of pyridine to the boiling hot solution. Cool, filter through a filtering crucible and wash as recommended in the above procedure. Dry in a vacuum desiccator and weigh. The factor for cadmium is 0.2063.

If only 1 ml. of pyridine is used for the precipitation of the cadmium salt,  $[\text{CdPy}_2](\text{SCN})_2$  is obtained.

Kragan<sup>103</sup> has suggested a procedure for the determination of cadmium based upon the formation of  $[\text{CdPy}_2]\text{Cl}_2$ , which is formed when pyridine is added to a solution of cadmium chloride. When this compound is heated in an air-bath at 120° C., 1 mole of pyridine is expelled. This precipitate may be used for the gravimetric determination of cadmium. The compound  $[\text{CdPy}_2]\text{Cl}_2$  may also be determined by an alkalimetric titration, using Patent Blue as an indicator.

**Separation of cadmium and mercury.** Cadmium is quantitatively precipitated with pyridine and a thiocyanate, while mercury similarly treated remains in solution. When an aqueous solution of mercuric chloride is treated with pyridine, a white crystalline precipitate of  $\text{HgCl}_2\text{Py}$  is formed, but this dissolves in an excess of pyridine. If  $\text{HgCl}_2\text{Py}$  is treated with an aqueous solution of potassium or ammonium thiocyanate it dissolves immediately due to the formation of a complex ion with mercury. This is shown in the following equation:

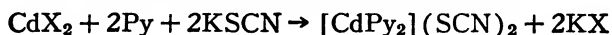


This difference in the behavior of cadmium and mercury salts in the presence of pyridine and thiocyanates makes possible a quantitative separation of these metals.<sup>82,104</sup>

**Procedure.** Add an excess of ammonium thiocyanate to a neutral solution containing cadmium and mercury salts and heat gently. Cool and add a slight excess of 1:3 pyridine and allow the mixture to stand for at least 1 hour. Decant off the clear supernatant liquid and wash the cadmium precipitate with water containing ammonium thiocyanate and pyridine. The precipitate usually contains a little mercury. Redissolve in a little N hydrochloric acid, neutralize with ammonia until the odor of pyridine is detectable, and then repeat the precipitation. Dissolve the precipitate in dilute nitric acid, evaporate with sulfuric

acid to destroy the organic matter, and weigh the cadmium as cadmium sulfate in a quartz crucible. Mercury can be determined in the combined filtrates by precipitation as mercuric sulfide.

**Titrimetric determination of cadmium.** Cadmium, like other metals which are precipitated with ammonium thiocyanate and pyridine, can be determined titrimetrically by precipitating with a known excess of a standard thiocyanate solution, and then titrating the excess with standard silver nitrate solution.<sup>105-107</sup> The determination is based on the reaction:



**Procedure.** Place the solution to be analyzed in a 100-ml. volumetric flask and add a measured volume of standardized 0.1 N potassium thiocyanate. This should be a quantity in excess of that required for the precipitation of the cadmium. Then add an excess of pyridine and mix well. Allow the mixture to stand until the precipitate has settled and dilute to the mark. Again mix well and filter through a dry filter paper. Neutralize an aliquot part of the solution with dilute nitric acid to an end-point with  $\alpha$ -dinitrosophenol, and then add 20 drops of a 1 per cent alcoholic solution of diphenylcarbazone, and titrate with a standardized 0.1 N silver nitrate solution to the appearance of a violet color. One ml. of 0.1 N KSCN = 0.00562 g. of Cd.

**Detection and determination of manganese.** Manganous salts react with pyridine and potassium dichromate to give a difficultly soluble salt, which possesses a recognizable crystalline form.<sup>5,6</sup> Korenman<sup>7</sup> has used this reaction for the microchemical identification of manganese. Since many other elements also yield precipitates with pyridine and potassium dichromate, the reaction seems to be of little analytical value. If an alkaline solution of a manganous salt is treated with an alkali thiocyanate and an excess of pyridine, manganese is precipitated as  $[\text{MnPy}_4](\text{SCN})_2$ . This precipitate can be weighed after suitable washing and drying. This reaction may be used as the basis for an accurate and rapid method of determining manganese.<sup>108,109</sup>

**Procedure.** To 50-100 ml. of a neutral solution containing not more than 0.6 g. of manganese, add 1.5 g. of solid ammonium thiocyanate and 4 ml. of pyridine at room temperature. Stir the mixture for 2-3 minutes and filter off the precipitate of  $[\text{MnPy}_4](\text{SCN})_2$ . Transfer this precipitate to a filter crucible with a solution prepared by dissolving 20 g. of ammonium thiocyanate and 80 ml. of pyridine in a liter of water. Then wash the precipitate with 15 ml. of 15 per cent alcohol containing 5 g. of ammonium thiocyanate and 100 ml. of pyridine per liter, and then with 10 ml. of 15 per cent pyridine in 95 per cent alcohol, and finally with 15 ml. of ether containing 2 drops of pyridine. Dry in a vacuum desiccator to constant weight. The factor for manganese is 0.1127.

Ammonium acetate interferes with this determination, but other ammonium salts are harmless.

**Detection and determination of antimony.** Alkalies and organic bases form highly colored insoluble iodoantimonates and iodobismuthates of the gen-

eral formula  $B \cdot HI \cdot MI_3$  (in which  $B$  = base and  $M$  = bismuth or antimony) when added to an acid solution containing bismuth or antimony salts and potassium iodide. This reaction has been used by Caille and Viel<sup>110,111</sup> for the detection of bismuth and antimony. Quinoline and antipyrine have generally been used as the organic base in this reaction, although pyridine can be substituted with fairly satisfactory results. A number of colorimetric methods for the determination of small quantities of antimony have been based upon the formation of the yellow color obtained when organic bases are added to solutions containing antimony and potassium iodide, but those using pyridine appear to be most satisfactory. Antipyrine, for example, cannot be used in such a procedure, although it gives a highly colored antimony compound. Pyridine is more satisfactory because the compound obtained is more soluble than that with antipyrine.<sup>112</sup>

Clarke<sup>112</sup> has used the golden yellow color which is produced with antimony and potassium iodide in the presence of pyridine for the colorimetric determination of small quantities of antimony. The yellow pyridine antimony iodide is kept in suspension with the aid of gum arabic.

**Procedure.** Add the following reagents in the order named to a 100-ml. Nessler tube: 10 ml. of 1 per cent gum arabic, 5 ml. of 20 per cent potassium iodide, 1 ml. of 10 per cent aqueous pyridine, 1 ml. of a one-tenth saturated sulfur dioxide solution, 60 ml. of cold 1:3 sulfuric acid, and then add 20 ml. of the solution to be analyzed, which should contain approximately 0.05-2.5 mg. of antimony. Transfer the solution to be analyzed with the aid of not more than 5 ml. of water and stir the mixture thoroughly with a glass rod. Into a second Nessler tube place the same reagents and in the above order except that 80 ml. of 1:3 sulfuric acid should be used instead of 60 ml. as above, and then add slowly a standard antimony solution containing 0.1 mg. of antimony per ml. until the colors match after the solution has been well stirred. A final adjustment is made just before the final matching by adding water to make the volume in the two tubes equal. It is best to view the tubes vertically over a white tile inclined at an angle to act as a reflector. The standard antimony solution contains 0.2764 g. of tartar emetic in 1,000 ml. of 10 per cent sulfuric acid.

Tin and arsenic in moderate quantities produce no color with pyridine and potassium iodide and do not interfere with this determination. Bismuth and several of the heavy metals yield colored precipitates and must be absent. Zinc also interferes by forming a white crystalline precipitate. The above method has been found particularly useful for the determination of small quantities of antimony in tin after separating the antimony from all interfering metals.

Chloride ion decreases the color intensity or destroys the color entirely. The maximum color intensity is attained in a solution which is 6 to 8 N in sulfuric acid. The iodide concentration should correspond to 1 per cent potassium iodide in the final solution. Too much pyridine bleaches the color. Alkali sulfates are without effect. The formation of iodine by atmospheric oxidation is prevented by the addition of a small quantity of sulfurous acid. Only a very little of the latter should be used, however, since otherwise a yellow color may be formed.

Vasil'ev and Shub<sup>118</sup> have used a modification of Clarke's method<sup>112</sup> for the determination of antimony in copper. They have introduced some new details in the method of separating antimony from interfering substances, and instead of comparing the color of the aqueous solution produced by the reaction of antimony, pyridine and potassium iodide, they recommend the extraction of the yellow organic compound with amyl alcohol and the measurement of the color of this solution.

Shapiro<sup>114</sup> has applied the method of Clark to the determination of from 0.03 to 3.0 per cent antimony in mercury ores containing up to 8 per cent mercury, 10 per cent of iron and 5 per cent of arsenic. In this procedure gelatin is used to replace the gum arabic to prevent the flocculation of the antimony compound. Fainberg<sup>115</sup> has used a similar procedure for the determination of antimony in refined lead.

**Determination of bismuth.** Ostroumov<sup>116</sup> has based a method for the determination of bismuth in the presence of lead, copper and cadmium upon the precipitation of bismuth with a mixture of pyridine and pyridine nitrate.

**Procedure.** Heat 100 ml. of the solution containing bismuth, cadmium, and copper salts to about 80° C. and slowly neutralize with a 10 per cent solution of ammonia. Add concentrated nitric acid dropwise until the solution is clear and add 6-8 g. of ammonium nitrate. Heat the mixture to boiling. Remove from the burner, and while shaking add dropwise 20 ml. of a solution prepared by mixing 20 ml. of 6 N nitric acid with 34 ml. of pyridine and diluting to 1 liter. Again heat to boiling and allow the mixture to settle for 30-40 minutes and filter without further cooling. Wash the precipitate with a hot 3 per cent solution of ammonium nitrate containing 1 per cent by volume of the precipitating solution. Dissolve the precipitate in hot 6 N nitric acid diluted with an equal volume of water, and evaporate the solution to dryness on a water bath in a platinum cup. Moisten the residue with 1-2 ml. of water, add 5-10 drops of 10 per cent ammonia, and again evaporate to dryness. Repeat this treatment in order to remove the pyridine completely. Ignite slowly to constant weight, and weigh as  $\text{Bi}_2\text{O}_3$ . If less than 0.1 g. of lead is present, reprecipitation of bismuth is not necessary.

Excellent results are claimed for this method.

**Precipitation of aluminum and chromium and other metals.** Chromium and aluminum, like ferric iron, are quantitatively precipitated as the hydroxides upon the addition of an excess of pyridine to aqueous solutions of their salts.<sup>57,61,86</sup> A comparison of pyridine and ammonia as precipitants for these metals shows that ammonia affords a more complete precipitation, but precipitation with pyridine in the absence of zinc and sulfate is quantitative if a concentrated solution of pyridine is slowly added and the precipitate is filtered after standing for 24 hours. The precipitate obtained by using ammonia contains metals of the fourth analytical group in considerable quantity due to adsorption, but the precipitate formed with the aid of pyridine is relatively much purer.<sup>61</sup> The greater purity of the precipitate is a justification for the use of pyridine as a precipitant for these metals. In addition, the fact that pyridine can be used

to remove aluminum, chromium and iron before detecting or determining other metals by means of the formation of pyridine-thiocyanate or pyridine-halide complexes often makes the use of this reagent as a precipitant more desirable than ammonia.

**Precipitation of uranium, zirconium and tin.** Uranium is precipitated completely as  $\text{H}_2\text{U}_2\text{O}_7$  by means of pyridine. This compound can be ignited and weighed as  $\text{U}_3\text{O}_8$ . This reaction affords a convenient method for the separation of uranium from the alkaline earths.<sup>117</sup> The use of pyridine rather than ammonia, which is frequently used for the precipitation of uranium, offers two distinct advantages: the pyridine base is so slightly ionized that it does not form a carbonate or uranate, and there is less danger of incomplete precipitation or of contamination of the precipitate with the alkaline earth carbonates. The following procedure may be used for the precipitation:

**Procedure.** Add a few drops of methyl red indicator to a slightly acid solution containing a uranium salt, and add the 20 per cent pyridine solution until the mixture is neutral to the indicator. Add an additional 10 ml. of the pyridine solution. Heat on a hot plate until the precipitate has settled and the supernatant liquid becomes clear, and then add more pyridine if the indicator shows that the solution has become acid. Filter and wash the precipitate with 3 per cent ammonium nitrate solution containing a little pyridine. Ignite and weigh as  $\text{U}_3\text{O}_8$ .

The presence of ammonium chloride or ammonium nitrate is desirable, but large quantities of ammonium sulfate prevents the precipitation of uranium. When sulfate is present it is necessary to add about 30-40 ml. of pure pyridine for each 0.1 g. of  $\text{U}_3\text{O}_8$  in place of the 20 per cent solution recommended in the above procedure.

Kaufman<sup>118</sup> has studied the use of pyridine for the determination of uranium and for its separation from the alkaline earth metals and has found that a complete separation is obtained only if ammonium nitrate is added to the solution from which the precipitation takes place. He has also found that the presence of carbon dioxide in the pyridine solution has no effect upon the determination.

A 20 per cent solution of pyridine can also be used advantageously in place of ammonia for the precipitation of zirconium and tin. The precipitate so formed is less likely to be contaminated with manganese, cobalt and nickel if these cations are present, and a single precipitation is sufficient for a complete separation in the presence of these metals.<sup>119</sup> In precipitating zirconium and tin with pyridine, the formation of highly dispersed basic salts may be eliminated by the addition of 5-10 g. of ammonium chloride for every 100 ml. of solution.<sup>57</sup>

Zirconium, thorium, cerium, lanthanum, neodymium and praseodymium are also quantitatively precipitated from aqueous solutions of their salts by treating with pyridine.<sup>152</sup>

**Detection of gold.** Douglass and Gillies<sup>120</sup> have described a field test for gold which is based upon the formation of a gold mirror. This method, however, is not satisfactory in most cases, due to the formation of a dense precipitate

which obscures the mirror. A new method has been proposed by Douglass and Pearce:<sup>121</sup>

**Procedure.** Grind the ore to be examined to a fine powder and place 0.5 g. of the material in a test tube. Add 5 ml. of aqua regia, shake for 1 minute, and allow to stand for 0.5-1 minute. Withdraw 1 drop of this solution and place on a glass plate. Place a drop of a solution prepared by mixing 1 ml. of pyridine with 9 ml. of hydrobromic acid on the same plate in such position that the 2 drops almost, but not quite, touch. Then join the 2 drops and allow to stand undisturbed for 30 minutes. If gold is present, minute red crystals form around the margin of the drops after they evaporate. Clear crystals denote the presence of lead and possibly zinc.

Martini<sup>122</sup> has based a method for the microchemical detection of gold upon the formation of pyridine bromoaurate. By this method, as little as 0.02% of gold can be detected.

**Determination of germanium.** Germanium salts react with ammonium molybdate to form germanomolybdic acid. The pyridine salt of this acid is very insoluble and can be used for the quantitative separation of germanium. On the addition of ammonium molybdate and pyridine nitrate to a solution of germanium that has been acidified with nitric acid, a yellow precipitate is formed which corresponds in composition to the formula  $\text{Py}_4\text{H}_4[\text{Ge}(\text{Mo}_2\text{O}_7)_6]$ .

Geilman and Brunger<sup>123</sup> have used this reaction for the gravimetric determination of germanium in organic substances.

**Procedure.** Digest 2-5 g. of the dry material to be analyzed with 5 ml. of concentrated sulfuric acid and a small quantity of nitric acid until a light colored solution is formed. Boil off the excess nitric acid and cool, and then add 10 ml. of water, and again boil until white fumes of sulfur trioxide appear. Distill the germanium as germanium chloride from a hydrochloric acid solution in a current of carbon dioxide. Collect the distillate in a vessel containing 1 ml. of 3 N hydrochloric acid and surrounded by ice. The first 10 ml. of the distillate usually contains all the germanium. If the material to be analyzed also contains arsenic or selenium, the distillation of the germanium chloride is carried out in a stream of chlorine instead of carbon dioxide. Precipitate germanium as germanium sulfide by saturating the cold solution with hydrogen sulfide. Allow to stand overnight and collect the precipitate in a centrifuge.

Oxidize the germanium sulfide precipitate with hydrogen peroxide and ammonia, and to the neutral solution (which should have a volume of about 50 ml.), add 10 ml. of a 50 per cent solution of ammonium nitrate, 15 ml. of 3 per cent ammonium molybdate solution and 10 ml. of nitric acid ( $d = 1.2$ ). Warm on a water-bath until the mixture turns yellow, and then add 12-20 ml. of a saturated aqueous solution of pyridine nitrate. A milky white precipitate forms, and this becomes crystalline and turns yellow on standing for a short time. Allow the precipitate to settle and test for completeness of precipitation by adding 2-3 drops of pyridine nitrate to the clear supernatant liquid. Filter through a filter crucible, and wash with 50 ml. of a solution prepared by dissolving 12 g. of ammonium nitrate,

10 g. of nitric acid ( $d = 1.2$ ), and 0.5 g. of pyridine nitrate in 250 ml. of water. The precipitate is dried to constant weight and weighed. The weight of germanium is found by multiplying the weight of the precipitate by 0.0353.

The results obtained using this method with known quantities of germanium are shown in Table 2.

TABLE 2.—DETERMINATION OF GERMANIUM AS PYRIDINE GERMANOMOLYBDATE

Ge Used mg.	Wt. of Pyridine Precipitate mg.	Ge in Precipitate Using Factor 0.0353 mg.	Error
0.435	11.8	0.417	—0.018
0.838	23.8	0.840	+0.002
1.347	38.2	1.348	+0.001
1.802	50.2	1.783	—0.019
2.270	64.3	2.270	0.000
5.637	160.7	5.672	+0.035
10.284	284.9	10.057	—0.227

Davies and Morgan<sup>124</sup> claim that the above procedure is not entirely satisfactory and that better results are obtained when the pyridine is replaced by cinchonine.

**Detection of vanadium.** A solution of vanadyl sulfate reacts with a saturated solution of ammonium molybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , to give an amorphous precipitate which soon changes to a definite violet-blue crystalline compound on the addition of pyridine. By means of this reaction as little as 1  $\gamma$  of vanadium can be detected. No definite formula has been proposed for the vanadium compound.<sup>125</sup>

Katzoff and Roseman<sup>160</sup> have prepared a crystalline pyridinium vanadate having the formula  $(\text{C}_5\text{H}_5\text{N})_3\text{V}_5\text{O}_{14} \cdot \text{H}_2\text{O}$ . This is an orange colored, crystalline solid. It is practically insoluble in ether, alcohol, acetone and benzene, but it dissolves in water to form an orange colored solution. The compound is formed as follows:

**Procedure.** To a solution of a metavanadate, add one fifth of its volume of a cool 2:1 mixture of pyridine and concentrated hydrochloric acid. Add an equal volume of alcohol and cool. Precipitation is nearly complete.

Berisso<sup>166</sup> has found that Zwikker's reagent, which is prepared by mixing 4 ml. of 10 per cent copper sulfate solution with 1 ml. of pyridine and 5 ml. of water, yields characteristic prismatic crystals with 0.001-0.0002 M solutions of vanadyl sulfate. These crystals are probably a vanadium cupirpyridine.

**Reactions of the platinum metals.** Whitmore and Schneider<sup>126</sup> have studied the use of pyridine hydrochloride as a reagent for the micro-detection of

metals of the platinum group. The results obtained by the addition of a solid fragment of pyridine hydrochloride to a drop of a 1 per cent solution of platinum metal salts is shown in Table 3.

TABLE 3.—REACTIONS OF PLATINUM METALS

Test Material	Description
RuCl <sub>3</sub>	Very small reddish-brown granules form around the circumference of the drop. These granules are of such a small size that no distinct crystalline form can be distinguished.
RhCl <sub>3</sub>	No apparent reaction.
PdCl <sub>2</sub>	Crosses and radiating clusters of slender prisms form at once. On standing small dark crystals develop on these forms at right angles to the long axis of the slender crystals.
Na <sub>2</sub> OsCl <sub>6</sub>	On standing, bright-yellow, irregular crystalline structures appear at the edge of the drop. No definite crystalline form can be recognized.
IrCl <sub>3</sub>	Long, deep red, irregular forms develop around the circumference of the drop growing to a considerable distance into the drop. Also small spindle shaped crystals form near the circumference.
H <sub>2</sub> PtCl <sub>6</sub>	Large, bright yellow, irregular forms develop. These occur as radiates and appear to be made up of flat hexagonal plates.
AuCl <sub>3</sub>	A dense yellow precipitate forms immediately around the test particle. This precipitate is made up of a mass of long, slender, yellow crystals with rough serrated edges. These form an entangled mesh about the particle. Some slender prisms as radiating clusters are also formed.

**Detection of Thallium.** Martini<sup>153</sup> has used a solution of Martius yellow in pyridine as a microchemical reagent for thallium. The test is sensitive to 0.04γ of thallium.

**Detection of silver.** Solutions of silver salts react with concentrated aqueous solutions of potassium dichromate and pyridine to yield orange-colored crystalline compounds which can be used for the microchemical detection of silver.<sup>5-7,151</sup> The compounds correspond in composition to the formulas [AgPy<sub>3</sub>]<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and [AgPy<sub>2</sub>]<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. These salts possess recognizable crystalline forms.

A 2 per cent solution of dithizone in pyridine has been used as a microchemical reagent for silver.<sup>168</sup> The test is best carried out in a dilute nitric acid solution of pH 0.5-1.0. The microcrystals are specific even in the presence of lead and mercury.

**Separation of lithium from the alkali metals and barium.** With the exception of lithium chloride, the alkali chlorides and barium chloride are insoluble in anhydrous pyridine. Ammonium chloride also becomes soluble if 3 per cent of water is added to the pyridine, although this does not affect the solubility of the other chlorides. The solubility curve for lithium chloride in anhydrous pyridine shows a maximum at 28° C., and at higher temperatures there is a decreased solubility up to 80° C. With 97 per cent pyridine there is no such



transition point. The solubility of lithium chloride in anhydrous and 97 per cent pyridine is shown in Table 4.

TABLE 4.—SOLUBILITY OF LITHIUM CHLORIDE IN g. PER 100 ml. OF PYRIDINE

Temperature	Anhydrous Pyridine	Temperature	97 Per Cent Pyridine
8°	12.71	22°	14.31
20°	13.39	32°	15.98
28°	13.47	45°	18.46
40°	13.10	58°	20.08
49°	12.90	72°	20.66
60°	12.84	97°	22.48
80°	13.27		
100°	14.98		

The separation of lithium chloride from sodium chloride, potassium chloride, rubidium chloride, cesium chloride and barium chloride, based upon the solution of lithium chloride in pyridine, gives excellent results both with anhydrous and 97 per cent pyridine.<sup>127,128</sup> The following procedure is used:

**Procedure.** Evaporate the aqueous solution of the chlorides just to dryness. Digest the residue, which should not weigh more than 2 g., for a few minutes with 25 ml. of pyridine at 100° C. Thoroughly break up the residue with a stirring rod and allow the mixture to settle. Decant the clear liquid through a filter and wash two times with small quantities of pyridine. Dissolve the residue in a small quantity of hot water and evaporate just to dryness and then repeat the pyridine extraction. Combine the pyridine filtrates, distill off the pyridine, and convert the lithium chloride to lithium sulfate in the usual manner and weigh.

The maximum error for this procedure is -0.5 mg. of lithium chloride for 0.155 g. of the salt. For the other chlorides it is +0.8 mg. with 0.436 g. of the salts. The greatest source of error in this procedure is due to the occlusion of lithium chloride by crystals of the chlorides of the other metals.

The method for separating lithium from sodium and potassium using alcohol saturated with hydrogen chloride is difficult to carry out, and the amyl alcohol method of Gooch is simple and reliable but requires a correction for sodium and potassium chlorides. The pyridine method gives excellent results and does not dissolve sodium chloride or potassium chloride, even in traces.

**The detection and determination of phosphorus.** Pyridine dissolved in a solution of ammonium or potassium molybdate forms an extraordinarily sensitive reagent for phosphoric acid. A yellow precipitate is formed which can be used for the detection or determination of small quantities of phosphorus.<sup>129</sup>

**Procedure.** Place a solution containing about 0.1 g. of  $P_2O_5$  in a 200 ml. volumetric flask and dilute to the mark. Mix well and withdraw 20 ml. of this

solution (about 0.01 g.  $P_2O_5$ ) and mix with 30 ml. of a solution of potassium molybdate containing pyridine. Filter the voluminous yellow precipitate and wash with dilute sulfuric acid, and then dissolve in ammonia and again make acid. Precipitate the phosphorus with magnesia mixture and determine as magnesium pyrophosphate in the usual manner.

With this reaction as little as 0.01 mg. of  $P_2O_5$  in 10 ml. of solution can be detected. With magnesia mixture only 0.1 mg. in 10 ml. can be detected.

**Determination of tellurium.** Jilek and Kota<sup>180</sup> have proposed the use of pyridine for the precipitation of  $TeO_2$  in a procedure for the gravimetric determination of tellurium.

**Procedure.** Neutralize a hydrochloric acid solution containing not more than 0.2 g. of  $TeO_2$  with ammonium hydroxide until a permanent turbidity appears, and then just redissolve by the addition of 5 N hydrochloric acid. Dilute the mixture to 100 ml. and heat to boiling. Add dropwise a 1:3 pyridine solution to the reappearance of a faint turbidity, and then continue the addition of the pyridine solution at the rate of 1 drop every 4 seconds until the mixture is alkaline to methyl orange. Allow the mixture to stand for 12 hours and filter. Wash the precipitate and dry at 105-30° C. to constant weight. This precipitate is not hygroscopic, which is an advantage over the earlier methods proposed by Browning and Flint<sup>132</sup> and Clauder.<sup>133</sup> For quantities of less than 30 mg. of  $TeO_2$ , the volume of the solution should be 25 ml. The lower limit for the determination is 1.4 mg. of tellurium in 25 ml. of solution.

Results obtained by this method agree very closely with those based upon the reduction of the tellurium compounds to metallic tellurium.<sup>131</sup>

**Detection of arsenic.** Martini and Berisso<sup>134</sup> have used pyridine in a microchemical method for the detection of arsenic in forensic work.

**Procedure.** Treat the minced tissue with 20 parts of hydrogen peroxide and an equal volume of 30 per cent sodium hydroxide. The arsenic dissolves in about 15 minutes as sodium arsenate. Place a drop of this solution on a microscope slide and add a drop of 20 per cent cesium chloride solution, 1 drop of a cold saturated solution of disodium hydrogen phosphate, and a little pyridine. Colorless tetrahedra are formed if arsenic is present.

**Detection and determination of cyanide.** Hydrogen cyanide can be detected by its catalytic effect in promoting the reaction between ammonia and alloxan to form characteristic crystals of oxaluramide.<sup>162</sup> According to Deniges<sup>163</sup> the reaction is made more sensitive by substituting pyridine for ammonia.

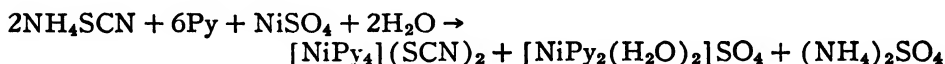
Aldridge<sup>170</sup> has developed a method using pyridine for the colorimetric determination of small quantities of cyanide. The cyanide is converted into cyanogen bromide by the action of bromine and water; and, after removing the excess bromine with sodium arsenite, the cyanogen bromide is made to react with a solution of benzidine in dilute pyridine. A deep orange or red color is

formed in this reaction, and this color is suitable for a colorimetric estimation. For the details of this procedure, see the section on benzidine.

**Detection and determination of thiocyanate and cyanates.** Thiocyanates may be detected and determined by means of the insoluble copper and nickel pyridine thiocyanates which are formed when pyridine and a copper or nickel salt is added to a solution of a thiocyanate.<sup>1,84</sup> The reactions employed for the detection or gravimetric determination of thiocyanates are very similar to those previously described in the sections on the determination of nickel and copper.

**Procedure.** Add an excess of a concentrated aqueous solution of a nickel salt and 10-20 drops of pyridine with stirring and at room temperature to the solution containing the thiocyanate, and after the blue precipitate forms, heat almost to boiling with stirring. Cool gradually to room temperature and decant the supernatant liquid from the precipitate. Wash free of the excess nickel salt with 5 per cent pyridine, dry in a porcelain crucible at 130° C., incinerate slowly, and heat with a blast lamp for 2-3 hours. To reduce traces of  $\text{Ni}_2\text{O}_3$  to  $\text{NiO}$ , the final heating must be carried out with a covered crucible.

From the final weight of  $\text{NiO}$ , the amount of thiocyanate can be calculated from the following equation:



When a cyanate is added to a solution of a copper salt containing a few drops of pyridine, a lilac-blue precipitate is formed which when dried becomes ultramarine in color. This compound has the composition  $[\text{CuPy}_2](\text{OCN})_2$ , and dissolves in chloroform with the formation of a sapphire-blue color. This reaction has been used by Werner<sup>185</sup> for the detection of cyanates.

**Procedure.** Add a few drops of pyridine to 2-3 drops of a 1 per cent solution of a copper salt in about 10 ml. of water, and then add 2 ml. of chloroform and the solution to be tested. Shake well. A sapphire-blue color appears in the chloroform layer if cyanates are present. This reaction is sensitive to 1 part of cyanate in 2,000 parts of solution.

With very dilute solutions of cyanates, an excess of the copper sulfate should be avoided. A small excess of pyridine promotes the solution of the blue complex.

Cyanates can also be detected by means of the colored complexes which are formed with nickel, cobalt and zinc salts and pyridine.<sup>186</sup> Bailey and Bailey<sup>187</sup> have proposed the following method for the colorimetric determination of cyanates and thiocyanates:

**Procedure.** If the solution to be analyzed is strongly acid or alkaline, it should be made neutral or faintly acid by means of ammonia or acetic acid. Add 1.5-2.0 ml. of 20 per cent pyridine to a measured volume of the solution to be determined, and then add a 0.2 per cent solution of copper sulfate until after agitating with chloroform a faint blue tint is perceptible in the aqueous layer. Extract several times with small portions of chloroform, filter, dilute to 10 ml. and compare in a colorimeter with a standard similarly prepared.

This method cannot be used in the presence of disodium phosphate, sodium tartrate, sodium thiosulfate, sodium nitrite, sodium sulfite, sodium cyanide or thiourea.

Aldridge<sup>170</sup> has developed a method using pyridine for the colorimetric determination of small quantities of thiocyanate. The thiocyanate is converted to cyanogen bromide by the action of bromine and water; and, after removing the excess bromine with sodium arsenite, the cyanogen bromide is made to react with a solution of benzidine in dilute pyridine. A deep orange or red color is formed in this reaction, and this color is suitable for a colorimetric estimation. For the details of this procedure, see the section on benzidine. Hydrogen cyanide and thiocyanic acid may be differentiated by the fact that the former is volatile on heating a slightly acid solution.

**Detection and determination of silica.** In acid solutions, silicic acid reacts with ammonium molybdate to give a precipitate containing 3 moles of  $\text{NH}_3$ , 1 mole of  $\text{SiO}_2$  and 12  $\text{MoO}_3$ . The formation of this yellow compound has been made the basis for several methods for detecting small quantities of silicic acid. This silicomolybdate forms insoluble precipitates with ammonia and many organic bases. The insoluble pyridine salt may be used for the detection and determination of silica.<sup>138</sup> The formation of the pyridine salt does not afford a satisfactory method for a gravimetric determination, for, although precipitation appears to be quantitative with only a slight excess of pyridine, a part of the precipitate dissolves in a larger excess of the reagent. Babko,<sup>139</sup> however, has used this reaction for the separation of silicic acid as a preliminary step in a titrimetric determination.

**Reagents.** *Pyridine hydrochloride reagent:* Mix 10 ml. of pyridine with 70 ml. of water and 20 ml. of concentrated hydrochloric acid.

*Pyridine wash solution:* Dissolve 10 ml. of pyridine and 20 ml. of concentrated hydrochloric acid in 1 liter of water.

**Procedure.** Neutralize a solution containing 3-5 mg. of silica, and boil with a small excess of sodium carbonate or potassium hydroxide. Heat the solution to 50-60° C. and treat with 5 ml. of a 10 per cent solution of ammonium molybdate, and then acidify with hydrochloric acid. Precipitate the silicomolybdic acid by adding 10 ml. of the pyridine hydrochloride reagent. Filter off the precipitate, wash 4-5 times with a cold 1 per cent pyridine hydrochloride solution, and then with hot water. Dissolve the washed precipitate in 50 ml. of 1:4 sulfuric acid, heat the resulting solution, and pass through a cadmium reductor. Then titrate the molybdenum in the solution with a 0.1 N solution of potassium permanganate. 1 ml. of 0.1 N potassium permanganate corresponds to 0.1667 mg. of  $\text{SiO}_2$ . This method is said to be very accurate.

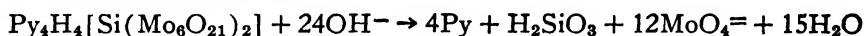
The pyridine silicomolybdate precipitate may also be determined by a neutralization process. In this procedure, the precipitate, after washing with pyridine hydrochloride, is washed several times more with a saturated solution of sodium or potassium chloride containing 1-2 per cent pyridine. It is then dissolved in a measured excess (10-20 ml.) of 0.1 N sodium hydroxide, and the excess

titrated with 0.1 N hydrochloric acid, using phenolphthalein as the indicator. 1 ml. 0.1 N hydrochloric acid corresponds to 0.25 mg. of  $\text{SiO}_2$ .

Mika<sup>185</sup> has used the following method for the titrimetric microdetermination of silicon in steel:

**Procedure.** To a hot solution of 100 mg. of steel in dilute nitric acid, add ammonium molybdate and keep the temperature at  $90^\circ$  for 5 minutes. Mix with a solution of pyridine that has been made acid with nitric acid. Cool, filter, and wash the precipitate with dilute potassium nitrate solution. Dissolve the washed precipitate in a measured volume of 0.1 N sodium hydroxide solution. Add 0.1 ml. of 0.1 per cent phenol red solution, and add 0.1 N sodium hydroxide until the brownish-red color does not change back to yellow, even on heating several minutes.

The probable reaction is:



Thus, 1 atom of silicon is equivalent to 24  $\text{OH}^-$ .

**Detection and determination of the halogens.** Bromides may be differentiated from chlorides by the use of a pyridine-copper sulfate solution, prepared by mixing 4 ml. of a saturated aqueous solution of copper sulfate with 1 ml. of pyridine. Crystals of the alkali bromides and chlorides when added to this solution yield distinctive crystalline forms.<sup>140</sup>

Since thiocyanates interfere with many of the analytical tests for chlorides and bromides, it is frequently necessary to provide methods whereby this interference can be eliminated. One convenient method for accomplishing this depends upon the precipitation of the thiocyanates by means of a mixture of pyridine and a copper or nickel salt.<sup>141,142</sup>

**Procedure.** Add 8-10 drops of pyridine and an excess of a neutral copper sulfate solution to a neutral solution containing chlorides, bromides and thiocyanates. The complex copper pyridine thiocyanate is filtered off, and chlorides and bromides are detected in the filtrate by the usual reactions.

A similar method is used for the separation of chlorides and thiocyanates as a preliminary to the titrimetric determination of chlorides.<sup>143</sup>

When titrating an iodide with a solution of mercuric nitrate, using diphenylcarbazide as the indicator, an excess of the mercuric ion is shown by violet color. In the presence of much mercuric iodide, however, some difficulty is experienced in observing the end-point of the titration. To avoid this, a little pyridine is added to the titration mixture which causes the formation of a white colloidal precipitate with mercuric iodide. For titrating 12-126 mg. of iodide, use 2 ml. of 2 N nitric acid in 50-100 ml. of solution, and add 7 ml. of 10 per cent aqueous pyridine before titrating.<sup>144</sup>

Spacu and Armeanu<sup>145</sup> have used pyridine as an aid in the detection of chloride, bromide and iodide in the presence of selenocyanates,  $(\text{SeCN})^-$ .

**Procedure.** Add 10 g. of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  or  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  dissolved in 35 ml. of water, and 10 ml. of pyridine to a dilute aqueous solution to be tested

and shake vigorously. Cool to 15° C. and filter off the sky-blue precipitate of  $[\text{NiPy}_4](\text{SeCN})_2$ . The halogens may be detected in the filtrate by any of the usual reactions.

About 2 mg. of potassium selenocyanate remains in the filtrate, but this does not interfere with the usual analytical procedures for halogens. The blue color may be extracted, however, with chloroform or carbon disulfide if necessary.

**Detection of permanganate, chromate, dichromate, thiosulfate, persulfate, perchlorate.** A solution prepared by mixing 4 ml. of 10 per cent copper sulfate, 1 ml. of pyridine and 5 ml. of water (Zwicker's reagent) yields characteristic crystals with permanganate, chromate, dichromate, thiosulfate, persulfate and perchlorate.<sup>8,146,147</sup> By means of these reactions, chromates and permanganates can be detected at a dilution of 1:20,000 and dichromates at a dilution of 1:10,000.

Spacu<sup>147</sup> has based a method for detection of persulfates upon the formation of the slightly soluble blue salt  $[\text{CuPy}_4]\text{S}_2\text{O}_8$ .

**Procedure.** To 15 ml. of the solution to be tested, add 5-10 drops of 20 per cent copper sulfate with stirring and sufficient pyridine to impart a blue color to the solution. A blue precipitate appears if persulfate is present. By means of this reaction, persulfate can be detected at a concentration of 0.16 g. per liter.

**Detection and determination of chlorate.** Pyridine in concentrated sulfuric acid gives a permanent violet color with chloric acid, and this reaction can be used for the detection or approximate determination of small quantities of chlorate.<sup>148</sup>

**Procedure.** Place 3 ml. of pyridine in a test tube and add 9 ml. of concentrated sulfuric acid dropwise and then cool. Carefully evaporate a solution of a chlorate to dryness in a small porcelain dish, and to the residue add 1 or 2 drops of the pyridine-sulfuric acid mixture. A violet color appears if chlorate is present.

A somewhat similar procedure is used for determining the chlorate content of weed-killers, and for the determination of chlorates in nutrient water cultures. Nitrates, chlorides, sulfates and phosphates do not interfere.

**Detection of free sulfur.** When a solution of sulfur in pyridine is made basic with sodium hydroxide, a blue-green, olive-brown or brownish-red color results. This reaction is useful for the detection of small quantities of sulfur.<sup>50</sup> As little as 0.01 mg. of sulfur per ml. of solution can be detected in this way. Free sulfur in ultramarine, rubber, drugs, and insecticides can be determined colorimetrically by the following procedure:<sup>52</sup>

**Procedure.** Extract the material to be analyzed with pure, water-clear pyridine. Filter, and add to the resulting solution one-tenth its volume of 2 N sodium hydroxide solution, and then compare the resulting color with that of pyridine solutions treated similarly, and which contain known quantities of sulfur.

**Detection of rhenium.** Rhenium chloride dissolves in solutions of hydrochloric acid to form chlororhenic acid. This compound forms characteristic crystalline salts with pyridine. These crystals can be used for the microscopic detection of rhenium.<sup>58</sup>

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**2-BENZYLPIRIDINE** $C_{12}H_{11}N$ 

Beil. Ref. XX, 425.

Mol. Wt. 169.22



**Use:** Detection of sulfur dioxide and tin.

2-Benzylpyridine is a liquid having a citron-like odor. It boils at 276° C., and has a density of 1.0536. It is insoluble in water, but is soluble in alcohol and ether.

**Preparation:** 2-Benzylpyridine is prepared by heating 12 g. of pyridine with 30 g. of benzyl iodide or 16 g. of benzyl chloride in a tube to 250-270° C. The product is decomposed with sodium hydroxide.<sup>1</sup>

**Detection of sulfur dioxide and tin.** Freytag<sup>2-4</sup> has described a procedure for the detection of sulfur dioxide and tin in which 2-benzylpyridine is used.

**Reagent.** Shake 0.2-0.5 ml. of 2-benzylpyridine with 100 ml. of 96 per cent ethyl alcohol. Add 100 ml. of water, and again shake for 2 minutes. Place the mixture in a round-bottom flask of ordinary glass and expose it to the action of ultra-violet light. The rays of 300-350 mμ, which penetrate ordinary glass, are effective in the formation of the desired photo-product. The same result may be accomplished by bright sunlight, but the time required is about 8 days, whereas a Hanau lamp can accomplish the same result in one hour.

**Procedure.** To the solution prepared above, add 10 ml. of water, mix, and pour into a flat dish. Immerse filter paper in this solution so that it is uniformly wetted. Allow to remain there about 45 minutes and then hang in the bright sunlight until dry. The green reagent paper turns red in the presence of sulfur dioxide and stannous chloride. As little as 1 part of SO<sub>2</sub> in 28,000 parts of the gas gives the color change.

Feigl and Leitmeier<sup>5</sup> have studied this reaction and report that it is not practical, although Freytag insists that the test is satisfactory.

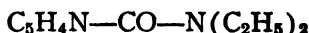
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**CORAMINE**

Synonym: Pyridine-β-carboxylic acid diethylamide

 $C_{10}H_{14}ON_2$ 

Mol. Wt. 178.21



**Use:** Detection of cobalt and copper.

Coramine is a yellow, almost odorless liquid. It is miscible with water. It is usually sold as a 25 per cent aqueous solution.

**Preparation:** Heat pyridine-2,3-dicarboxylic anhydride with diethylamine under reflux for two hours. Distil the excess diethylamine and heat the residue to 180° C. Distill the oily product *in vacuo*.

**Detection of copper and cobalt.** Martini<sup>1</sup> has used coramine for the microdetection of copper and cobalt.

**Procedure.** Add a drop of coramine and a drop of 5 per cent potassium thiocyanate to a little of the solution to be tested. Dissolve the white precipitate which forms in ammonium hydroxide and from this solution white or gray sheaf-like crystalline aggregates slowly separate. About 0.4γ of either metal may be detected by this reaction.

Zinc, cadmium and tin do not give similar reactions.

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### **α-PHENYLPYRIDINE**

C<sub>11</sub>H<sub>9</sub>N

Beil. Ref. XX, 424.

Mol. Wt. 155.19

C<sub>5</sub>H<sub>4</sub>N—C<sub>6</sub>H<sub>5</sub>

**Use:** Determination of platinum, and metals of the platinum group.

α-Phenylpyridine is a liquid boiling at 268.5-270.5° C. It is insoluble in water, but is soluble in alcohol and ether.

**Preparation:** Prepare benzenediazonium chloride in the usual manner and add to the equivalent quantity of warm pyridine. Make strongly acid with hydrochloric acid and extract with ether. Separate the aqueous solution, and make it strongly alkaline with sodium hydroxide, and again shake out with ether. Separate, and evaporate the ether extract, and then distill the basic oil which is obtained. Unchanged pyridine first distills over and then a pale yellowish oil is obtained which partially solidifies at approximately 0° C. Separate the solid by quickly filtering with suction and repeat the cooling and filtering as long as crystals separate. Crystallize the solid from hot water. The crystalline mixture consists of α- and γ-phenylpyridine. Dissolve the solid in alcohol and mix with a cold saturated solution of picric acid. Filter off the yellow precipitate which forms and dissolve in the least possible quantity of boiling alcohol. When the mixture is allowed to cool, the γ-phenylpyridine separates first, followed later by yellow needles of α-phenylpyridine picrate (M.P. 169-171°).<sup>1</sup>

Decompose the picrate with NaOH and fractionally distill. Retain the fraction boiling at 265-267° C.<sup>1</sup>

**Determination of platinum and metals of the platinum group.** α-Phenylpyridine reacts with solutions of platinum salts to form complex double salts. By

igniting these complex salts such as phenylpyridine chloroplatinate in a Pregl micro-muffle, metallic platinum is obtained. Meyer and Hoehne<sup>2</sup> report that results obtained in the analysis of platinum salts using this reaction are almost theoretical. The platinum compound is  $(C_{11}H_{10}N)_2[PtCl_6] \cdot 2H_2O$ .

1. R. Mohlau and R. Berger, *Ber.* **26**, 2003 (1893).

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### $\alpha$ -PICOLINE

Synonym: 2-Methylpyridine

$C_6H_7N$

Beil. Ref. XX, 234.

Mol. Wt. 93.12

$C_6H_4N-CH_3$

**Use:** Detection of cobalt, cyanate and iron.

$\alpha$ -Picoline is a colorless liquid which is found in coal tar and bone oil. It has a strong, unpleasant odor. It boils at 128-129° C. and has a sp. gr. of 0.950. It dissolves readily in water and is miscible with alcohol and ether.

**Detection of cobalt, iron and cyanate.**  $\alpha$ -Picoline may be used in place of pyridine in the reactions between cyanates, cobalt or iron.<sup>1</sup> For details of this procedure, see section on pyridine.

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### $\alpha$ -PICOLINE METHIODIDE

$C_7H_{10}NI$

Mol. Wt. 235.07

$CH_3-C_6H_4N(CH_3)I$

**Use:** Detection of bismuth.

$\alpha$ -Picoline methiodide is a white crystalline solid melting at 230° C. It is very slightly soluble in cold or hot water, and is only slightly soluble in cold alcohol, but it dissolves readily in hot alcohol. It is soluble in acetone and ether.

**Preparation:**  $\alpha$ -Picoline methiodide is prepared by mixing 2 moles of methyl iodide and 1 mole of  $\alpha$ -picoline in a large beaker. A spontaneous reaction takes place and may become rather violent. The mixture solidifies with the evolution of considerable heat. Allow the solid to dry in an acid-free atmosphere. No further purification of the compound is necessary, and it will keep indefinitely in a closed container.

**Detection of bismuth.**  $\alpha$ -Picoline methiodide is another of the nitrogen bases which gives a color reaction with bismuth salts and potassium iodide. The reagent has been found to be more sensitive, however, when used alone rather than with potassium iodide, which is usually an essential part of other reagents containing the nitrogen bases. The iodide ion, which is necessary for the formation of the red bismuth precipitate, is derived from the  $\alpha$ -picoline methiodide.

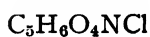
**Procedure.** If interfering substances are absent, the solution to be tested is made just acid to litmus with dilute hydrochloric acid. To 1 ml. of this solution, add 0.5-1 ml. of a solution prepared by dissolving 2.5 g. of  $\alpha$ -picoline methiodide in 10 ml. of water. An orange-red precipitate or an orange opalescence forms depending upon the concentration of the bismuth ion. The color obtained with the more dilute solutions of bismuth is best observed by looking vertically through the tube containing the reaction mixture.

By this method 0.002 mg. of bismuth can be detected in 1 ml. of solution. With concentrations of bismuth greater than 0.1 mg. per ml. an orange-red precipitate forms.

Silver, mercurous mercury, and lead may interfere by forming precipitates with the reagent, but this interference may be eliminated by completely precipitating the metallic ions with hydrochloric acid. The resulting mixture is then filtered, the filtrate neutralized with sodium hydroxide, and made acid with hydrochloric acid before applying the test. The excess hydrochloric acid does not interfere if the concentration of the bismuth ion exceeds 0.1 mg. per ml., but with lower concentrations of bismuth the test may fail in the presence of too much acid. Copper, ferric iron and other oxidizing substances interfere by converting the iodide to free iodine. This interference is best eliminated by treating the solution to be tested with potassium cyanide, and filtering off the solution of the complex cyanides from the precipitated bismuth hydroxide. The bismuth hydroxide is washed with potassium cyanide solution, and finally with cold water, and then dissolved in 2 N hydrochloric acid before adding the reagent. In the presence of antimony, stannous tin or large quantities of lead the regular separation for group IV should be used. Antimony is the most troublesome of interfering substances since it too yields a precipitate with the reagent. The crystals which first form are light yellow in color but these quickly coagulate to a reddish mass. The difference between the precipitate formed with antimony and that with bismuth is such that there need be no cause for confusion if only one of the ions is present; but in a mixture of these two metals, the orange-red crystals of the bismuth complex are obscured, and it is impossible to obtain a positive test without first removing antimony. Lead, mercurous mercury, silver and stannous tin form white to light yellow precipitates with  $\alpha$ -picoline methiodide. If the concentration of these ions does not exceed one-half that of the bismuth ion, and the concentration of the bismuth is at least 0.1 mg. per ml., no difficulty is experienced in carrying out the bismuth test.<sup>1</sup>

1. K. Whelan and F. J. Welcher, *J. Chem. Ed.* 20, 246-7 (1943); *C.A.* 37, 4320 (1943).

## PYRIDINIUM PERCHLORATE



Mol. Wt. 179.56



**Use:** Acidimetric standard.

Pyridinium perchlorate is a well crystallized solid, melting at 288° C. At 16° C.,

9.49 g. dissolves in 100 ml. of water, 0.454 g. dissolves in 100 ml. of absolute alcohol, and 1.2 g. in 100 ml. of 95 per cent alcohol.

**Preparation:** Mix pyridine, 1 equivalent of 6 N hydrochloric acid and 2 volumes of 6 N sodium perchlorate (perchloric acid can be used). Allow the mixture to stand for some time at 15° C. Filter, wash the precipitate with 20 per cent perchloric acid, and finally with absolute alcohol.

**Acidimetric standard.** Arndt and Nachtwey<sup>1</sup> have suggested the use of pyridinium perchlorate as an acidimetric standard. It is used in a boiling solution with phenolphthalein as the indicator. No great claim is made for the usefulness of this reagent beyond the fact that it may be obtained in high purity. Since the homologs of pyridine yield soluble perchlorates, perchloric acid is useful for preparing pure pyridine.

1. F. Arndt and P. Nachtwey, *Ber.* **59B**, 448-55 (1926); *C.A.* **20**, 2163 (1926).

## CHAPTER II

### QUINOLINE AND QUINOLINE DERIVATIVES

#### QUINOLINE

Synonym: Leucoline

$C_9H_7N$

Mol. Wt. 129.15

Beil. Ref. XX, 339.

**Use:** Detection of antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gold, indium, iridium, iron, lanthanum, lead, mercury, neodymium, nickel, osmium, palladium, platinum, phosphate, praseodymium, rhenium, silver, tin, thiocyanate, thorium, titanium, vanadium, zinc and zirconium.

Determination of cerium, lanthanum, neodymium, praseodymium, thorium and zirconium.

Quinoline is a colorless liquid, but becomes dark on standing. It possesses a characteristic odor, and absorbs moisture from air. It solidifies below  $-20^{\circ}$  and boils at  $239^{\circ}$  C. It is volatile with steam, and has a sp. gr. of 1.096. It is only slightly soluble in water, but is miscible with alcohol, ether, and carbon disulfide. The compound is basic and forms water-soluble salts with strong acids.

**Preparation:** Pour, with shaking, 45 ml. of concentrated sulfuric acid into a 1.5 liter flask containing 20 g. nitrobenzene, 31 g. of aniline, and 100 g. of anhydrous glycerol (obtained by heating commercial glycerol in a porcelain dish until a thermometer immersed in the liquid registers  $180^{\circ}$  C.). Fit the flask with a reflux condenser and heat on a wire gauge. Remove the flame as soon as a flow of bubbles indicates that the reaction has begun. Allow the reaction, which may become violent, to proceed without further heating until it subsides, and then apply heat and boil for 3 hours.

Next add a little water and remove the unchanged nitrobenzene with a current of steam. While the liquid is still warm, make alkaline with a concentrated solution of sodium hydroxide, and distill with steam the liberated quinoline (along with unchanged aniline). Extract the distillate with ether and evaporate the ether. Dissolve the crude compound in a mixture of 50 ml. of concentrated hydrochloric acid and 200 ml. of water. Warm and add 30 g. of zinc chloride in 50 ml. of 2 N hydrochloric acid. Cool in ice and collect the crystals by filtering with suction. Wash with cold 2 N hydrochloric acid, and decompose with concentrated sodium hydroxide. Distill with steam, extract the distillate with ether, dry the ether solution with solid potassium hydroxide, and, after removing the ether, distill at  $239^{\circ}$  C.<sup>1-3</sup>

**Precipitation of metals.** Quinoline reacts as a base to precipitate the hydroxides of many metals from aqueous solutions of their salts. Zirconium, thorium, cerium, lanthanum, neodymium and praseodymium may be precipitated quantitatively in this manner.<sup>25</sup>



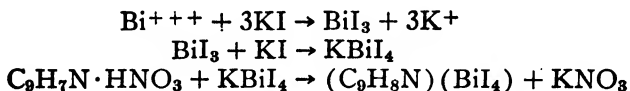
**Detection of bismuth.** An intense red-orange color is obtained when an alcoholic solution of quinoline and potassium iodide is added to a solution containing a bismuth salt. This reaction is suitable for detecting very small quantities of bismuth.<sup>4</sup>

**Reagent.** Dissolve 1 g. of quinoline in 100 ml. of alcohol and mix the resulting solution with 20 ml. of a 25 per cent solution of potassium iodide.

**Procedure.** Place a few drops of the solution to be tested on a spot plate. Acidify slightly and add a drop of sodium acetate solution, and then one drop of the quinoline reagent. An orange-red precipitate forms with bismuth. The sensitiveness of the reaction is 1:50,000.

A spot technique using filter paper saturated with the reagent detects 1.6γ of bismuth in one drop. The reagent gives with lead a yellow precipitate; mercury (ous), green; mercury (ic), white; silver, a very faint yellow; antimony, yellow; and with cupric and ferric ions, a brownish-red precipitate (due to the formation of iodine). If iron or copper is known to be present, place one drop of 10 per cent sodium bisulfite on the test paper saturated with the reagent and follow with one drop of acidified solution to be tested.

A somewhat different method for the detection of bismuth has been proposed by Ryazanov and Chekalina.<sup>5</sup> Potassium iodide is added to a bismuth solution until the precipitate of bismuth iodide is dissolved and transformed into the complex,  $\text{KBiI}_4$ . A 10 per cent solution of quinoline in 2 N nitric acid is then added to form a bright orange precipitate. This test is based on the following reactions:



The color of the bismuth complex depends on the concentration of the reagent, and on the concentration of the bismuth ion. Further, a decrease in the concentration of the bismuth salt has a greater effect on the color of the complex than a decrease in the concentration of the potassium iodide. Optimum results are obtained if equivalent amounts of potassium iodide and the bismuth salt are present. The colors of the precipitates obtained by the reaction of equivalent concentrations of potassium iodide and bismuth salt range from bright orange for concentrated bismuth solutions to a yellow turbidity for more dilute solutions.

The complex  $(\text{C}_9\text{H}_8\text{N})(\text{BiI}_4)$  dissolves in solutions of ammonium salts, and in sodium thiosulfate with decolorization. It also dissolves in cold hydrochloric acid, nitric acid, and sulfuric acid, and with ammonium hydroxide and sodium hydroxide it decomposes with the formation of a white precipitate. It is soluble in ether, and somewhat less soluble in alcohol. Free iodine is formed by atmospheric oxidation, or by oxidation with such reagents as bromine or chlorine water.

Quinoline also forms precipitates with mercuric mercury and cadmium and these ions may interfere, but the colors of these precipitates are not so bright as that of the bismuth compound. Silver; lead, mercurous mercury, copper, and

iron interfere. The first three of these interfere by the precipitation of the iodides, and the latter two by the oxidation of the iodide to free iodine. To remove this interference, add saturated sodium chloride until precipitation is complete, and add a solution of sodium pyrophosphate until the color disappears, and then add the quinoline nitrate dropwise. This reaction will detect 2.8γ of bismuth at a dilution of 1:360,000. A microchemical method for bismuth has been used by Gapchenko and Sheintzis.<sup>6</sup>

**Procedure.** Acidify the solution to be tested with nitric acid, and treat with a saturated solution of quinoline and a little ammonium thiocyanate. A golden-yellow, amorphous precipitate forms and quickly changes to x-shaped crystal groups.

The sensitiveness of this reaction is 0.3γ of bismuth in 0.001 ml. of solution. The test can be applied in the presence of all cations except zinc, tin (ous), antimony, mercury (ous), and silver. In the presence of cupric ions a drop of citric acid must be added before the test is applied.

**Reaction with copper.** An ammoniacal solution of copper containing ammonium thiocyanate yields with quinoline sulfate green monoclinic crystals of  $3(C_9H_7N-HCNS) \cdot [Cu(NH_3)_4](CNS)_2$ . These crystals may be used for the microdetection of copper.<sup>7</sup> When 7 ml. of quinoline is added to 4.82 g. of cupric nitrate an indigo compound is formed.<sup>8</sup> When dried at 50° C. the compound corresponds to the formula  $[Cu(NO_3)_2 \cdot 2C_9H_7N \cdot 2H_2O]$ .

**Detection of antimony.** Antimony salts in solution made slightly acid with hydrochloric acid yield a yellow precipitate when treated with potassium iodide and a solution of quinoline in 1:5 hydrochloric acid.<sup>23</sup>

**Detection of nickel.** The nickel compounds formed by the action of *o*-phenylenediamine or 1,3,4-toluylenediamine on an ammoniacal solution of a nickel salt are insoluble in ordinary organic solvents, but are partially soluble in quinoline with the formation of purple-colored solutions.<sup>9</sup> These reactions may be of some analytical value.

**Determination of thorium.** Quinoline may be used to determine thorium in monazite sand.<sup>10, 25, 26</sup> The monazite sand is digested with sulfuric acid, and thorium is later precipitated with ammonium oxalate in an alkaline solution. After filtering and dissolving the thorium precipitate in hydrochloric acid, thorium hydroxide is precipitated by adding quinoline to the boiling solution. This precipitate is then dissolved and the thorium again precipitated with ammonium oxalate. Thorium is finally determined by igniting the oxalate to  $ThO_2$ .

**Detection of arsenic.** Martini<sup>11</sup> has proposed a micromethod for the identification of arsenic, which may be used in forensic work.

**Procedure.** Cut sample to be analyzed into small pieces and treat with 20 parts of hydrogen peroxide and an equal volume of 30 per cent sodium hydroxide. Allow to stand 15 minutes to permit solution of the arsenic as arsenate. Place one drop of the resulting solution on a microscope slide, and add

one drop of concentrated hydrochloric acid. Mix, and add one drop of concentrated sodium iodide solution. Mix again, and finally add one drop of quinoline. Yellow-orange crystals of quinoline arsenate-iodide are obtained.

A general micromethod for arsenic may be carried out as follows:

**Procedure.** To the solution to be tested (containing  $\text{AsCl}_3$ ) add hydrochloric acid, sodium iodide, and one drop of quinoline. A powdery, orange-yellow precipitate of characteristic structure is obtained with arsenic.<sup>12</sup>

**Detection of rhenium.** Rhenium chloride dissolved in hydrochloric acid forms  $\text{HReCl}_4$ . This acid reacts with quinoline to form a crystalline compound that may be used for the microdetection of rhenium.<sup>13</sup>

**Separation of vanadium from chromium.** A reagent for separating vanadium from chromium is prepared by mixing 10 ml. of pure, synthetic quinoline with 20 ml. glacial acetic acid and diluting to 100 ml. with water. This reagent precipitates vanadate in the presence of chromate. The precipitate can be ignited to  $\text{V}_2\text{O}_5$ .<sup>14</sup>

**Detection of thiocyanate.** The formation of complex compounds containing a metal, thiocyanate, and an organic base may be used as a means of detecting the thiocyanate ion. With solutions of cobalt salts and quinoline, 0.5% of thiocyanate may be detected.<sup>15</sup>

**Microchemical reactions.** Martini,<sup>16,17,27</sup> Korenman<sup>18,19</sup> and Gapchenko and Sheintzis<sup>20</sup> have studied the use of quinoline and ammonium thiocyanate as a microchemical reagent. They report reactions with iron, zinc, cobalt, cadmium, bismuth, mercury, copper, lead, silver, tin, antimony and indium.

**Reagent.** A suitable reagent is prepared by mixing one part of quinoline and one part of a saturated aqueous solution of ammonium thiocyanate, and then adding dropwise dilute nitric acid until all quinoline is dissolved. The reagent should be freshly prepared. The results obtained with this reagent are shown in Table 5.

TABLE 5.

Ion	Description	Sensitiveness
Iron	Red crystals	0.3 $\gamma$
Zinc	Colorless	0.03 $\gamma$
Cobalt	Blue	.....
Cadmium	.....	3.0 $\gamma$
Indium	.....	0.04 $\gamma$

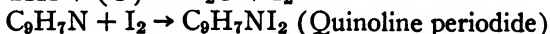
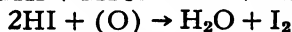
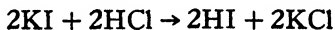
A somewhat similar reagent, in which potassium iodide is substituted for ammonium thiocyanate, may be used as a microchemical reagent. A summary of these reactions is given in Table 6, prepared by Korenman:<sup>19</sup>

TABLE 6.

Ion	Reagent	Description	Sensitiveness
Bi	Quinoline + KI + HCl	Dark brown or yellow orange	0.1–0.2γ
Sb	Quinoline + KI + HCl	Similar to bismuth	0.2–0.3γ
Sn	Quinoline + KI + HCl	Long yellow needles	3.0γ
Hg	Quinoline	Colorless needles	0.32γ
Cd	Quinoline + NaCl + acetic acid or H <sub>2</sub> SO <sub>4</sub>	Needles or rosettes	1.0γ
Cd	Quinoline + KI	Cryst.	0.1–0.15γ
Cu	Quinoline	Amorphous ppt. of hydroxide	
Cu	Quinoline + KI	Reaction is sensitive and characteristic (1 drop of Cu salt solution added to a neutral mixture of quinoline and KI yields characteristic crystals). A Cu HCl solution + quinoline + KI gives dark brown crystals. Sensitiveness: 0.15γ	0.05γ
Zn	Quinoline + KBr + HCl	Characteristic ppt.	0.5–0.6γ
Pb	Quinoline + KI + HCl		0.1γ

In general, the above tests were obtained by adding 1 drop of quinoline and one drop of potassium iodide solution to 1 drop of the acid solution to be tested.

The presence of a small quantity of an oxidizing substance in an acid solution of a mixture of quinoline with potassium iodide results in the following series of reactions:



Quinoline periodide and quinoline hydrogen iodide periodide,  $\text{C}_9\text{H}_7\text{N} \cdot \text{HI} \cdot \text{I}_2$ , are green in color. The periodide is insoluble and may cause some confusion in an analysis if oxidizing substances are present.

**Microdetection of titanium.** A method for the microdetection of titanium in minerals has been proposed by Martini.<sup>21</sup>

**Procedure.** Dissolve the mineral by suitable methods, and treat one drop of the resulting solution with an excess of concentrated hydrochloric acid, one drop of 20 per cent solution of ammonium thiocyanate, and finally with as much of a 1:50 solution of quinoline in 1:5 hydrochloric acid as will adhere to the point of a fine platinum wire. An orange or red color appears with titanium.

Crystals of the yellow iron, or of the blue cobalt compounds may be differentiated microscopically from those of titanium.

**Microdetection of chromium.** When one drop of 1 per cent chromic chloride solution is treated with one drop of a concentrated solution of oxalic acid and one drop of quinoline on a microscope slide, crystals of  $[\text{Cr}(\text{C}_2\text{O}_4)_2] \cdot$

$C_9H_7N$  are obtained. These may be identified with the aid of a microscope. By means of this reaction 0.01 mg. of chromium may be detected.<sup>22</sup>

**Detection of the platinum metals.** Whitmore and Schneider<sup>24</sup> have used quinoline hydrochloride for the microdetection of the platinum metals. As reagent they used a 10 per cent aqueous solution of quinoline hydrochloride. The results obtained with 1 per cent solutions of various salts of the platinum metals are given in Table 7, which is taken from the work of Whitmore and Schneider:

TABLE 7.—REACTIONS OF QUINOLINE HYDROCHLORIDE WITH SALTS OF THE PLATINUM METALS

Test Material	Description
RuCl <sub>3</sub>	No apparent reaction.
RhCl <sub>3</sub>	No apparent reaction.
PdCl <sub>2</sub>	A very fine yellow amorphous precipitate forms at once. Almost immediately throughout this mass there appear a great number of bright yellow, leaflike structures, singly, in pairs and in clusters.
Na <sub>2</sub> OsCl <sub>6</sub>	A dense brownish-yellow precipitate forms immediately. This precipitate is composed of minute crystals. Near the edge of the precipitate these arrange themselves in aggregates and small clusters.
IrCl <sub>4</sub>	A great number of reddish-brown X-shaped forms develop immediately throughout the entire drop. These forms are made up of long feather-like structures with rough, irregular edges.
H <sub>2</sub> PtCl <sub>6</sub>	Immediate formation of a mass of light yellow, X-shaped structures similar to those obtained with IrCl <sub>4</sub> . These form an entangled mass throughout the drop. At the circumference a few poorly formed yellow octahedra are also developed.
AuCl <sub>3</sub>	A dense mass of very slender light yellow, needle shaped crystals are formed immediately. These form an entangled mass throughout the drop. At the edge they develop into branching forms of considerable size.

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 **$\alpha$ -NAPHTHOQUINOLINE**

Synonym: 7,8-Benzoquinoline

 $C_{13}H_9N$ 

Mol. Wt. 179.21

Beil. Ref. XX, 463.

**Use:** Determination of bismuth and cadmium.

$\alpha$ -Naphthoquinoline is a crystalline solid which melts at 52° C. It is insoluble in water, but is soluble in organic reagents and dilute acids.

**Preparation:** Mix 170 g. of  $\alpha$ -naphthylamine, 80 g. of nitrobenzene, 300 g. of glycerol, 100 g. of glacial acetic acid and 300 g. of sulfuric acid and reflux for 24 hours. Pour the dark liquid into 3 liters of water and neutralize with about 300 g. of sodium hydroxide. Reflux the tar which separates with 1 liter of benzene, and extract the aqueous solution with benzene, and then combine the benzene extracts. Dry the benzene solution over sodium hydroxide, then remove the benzene by distillation, and finally distill the residue. Collect the fraction boiling at 300-342° C.

Dissolve this crude product in 2 liters of 1:3 hydrochloric acid, and add a solution of 40 g. of zinc chloride. Let stand, filter off the yellow precipitate and wash. Suspend in water and add 1 liter of 50 per cent sodium hydroxide solution with stirring. Separate the oil which forms and dry in ether. Remove the solvent and fractionate the residue. Collect the fraction boiling at 336-342° C.<sup>1,2</sup>

**Determination of bismuth.** In strong mineral acid solutions containing halide ions,  $\alpha$ -naphthoquinoline forms precipitates with mercury, bismuth, copper, cadmium, zinc, uranium and ferric iron. The stability and insolubility increase in the following order: chloride, bromide, iodide, thiocyanate. In the presence of chloride ions, only mercury and bismuth are precipitated. In solutions containing bromide or iodide, mercury, cadmium and bismuth are precipitated. In the presence of nitric or sulfuric acid, uranium and ferric iron precipitate as insoluble thiocyanates of  $\alpha$ -naphthoquinoline.  $\alpha$ -Naphthoquinoline is used for the micro- and macro-determination of bismuth. Good results are obtained, however, only

by a skillful operator, since strict attention to detail is essential. Bismuth is precipitated as  $(C_{13}H_9N) \cdot HBiI_4$ . The following procedure is recommended by Hecht and Reissner: <sup>3</sup>

**Reagent.**  *$\alpha$ -Naphthoquinoline solution:* Dissolve 2.5 g. of  $\alpha$ -naphthoquinoline in a mixture of 1.3 ml. concentrated sulfuric acid and 3 ml. of water and then dilute to 100 ml.

*Wash solution:* Mix 10 ml. of the  $\alpha$ -naphthoquinoline solution with 5 ml. of 0.1 N potassium iodide and 0.5 ml. of 10 per cent sulfurous acid and dilute to 100 ml.

**Procedure.** Bismuth should be present as bismuth sulfate in a solution containing 3 per cent of free sulfuric acid. If the bismuth is present as any other salt, or if any other acid is present, evaporate to dryness. Dissolve the residue in a little sulfuric acid and heat until fumes of sulfur trioxide appear. Dilute with a suitable volume of water. The volume of the bismuth solution should be such that after the addition of the reagent, the total volume for 10 mg. of bismuth is about 30 ml. For 10 mg. of bismuth, add 3-3.5 ml. of the 2.5 per cent solution of  $\alpha$ -naphthoquinoline and 0.5 ml. of 10 per cent sulfurous acid solution. Heat until the solution begins to boil, and then add 5-6 ml. of 0.2 N potassium iodide solution dropwise and with constant stirring. Boil for a short time and allow to cool. Filter through an  $A_1$  sintered glass crucible, and for 10 mg. of bismuth wash twice, using about 3 ml. of the wash solution. Use suction and wash with 5-6 ml. of cold water in small portions. Dry and weigh as  $(C_{13}H_9N) \cdot HBiI_4$ . The factor for  $Bi_2O_3$  is 0.2595.

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## $\beta$ -NAPHTHOQUINOLINE

Synonym: 5,6-Benzoquinoline, naphthoquinoline

$C_{13}H_9N$

Mol. Wt. 179.21

Beil. Ref. XX, 464.

**Use:** Detection of cadmium and zinc.

Determination of cadmium, germanium and tungsten.

$\beta$ -Naphthoquinoline consists of small white leaflets. It melts at 93-94° C. It is insoluble in water, but is soluble in alcohol, ether, benzene and dilute acids.

**Preparation:** Mix 100 g. of arsenic acid, 200 g. of concentrated sulfuric acid, 215 g. of glycerol and 100 g. of  $\beta$ -naphthylamine in a flask equipped with a reflux condenser. Slowly heat on an oil-bath until the reaction begins. The violence of the reaction is moderated by lifting the flask from the oil-bath. After the initial reaction has subsided, allow the mixture to boil gently for about 4 hours. Allow to cool somewhat and dilute strongly with water. Allow the mixture to stand for some time and filter off the precipitate. Then slowly add sodium

hydroxide solution until the mixture is alkaline. At this point the reagent separates as an oil, which soon solidifies as a crystalline solid. Boil the crystalline product for a short time in alcohol which contains a little animal charcoal and filter. Precipitate the pure reagent by mixing the alcoholic solution with water, or by allowing the alcoholic solution to drop into pure water. The reagent separates as a crystalline solid.<sup>1</sup>

**Determination of cadmium.**  $\beta$ -Naphthoquinoline has the same analytical properties as  $\alpha$ -naphthoquinoline (see above). Berg and Wurm<sup>2,7,8</sup> have proposed the use of  $\beta$ -naphthoquinoline as a reagent for the determination of cadmium. A precipitate of  $(C_{13}H_9N)_2 \cdot H_2CdI_4$  is formed when  $\beta$ -naphthoquinoline is added to a dilute sulfuric acid solution containing a cadmium salt and potassium iodide. The presence of tartrate and iodide prevents the precipitation of tin or antimony with cadmium.

**Reagent.** Dissolve 2.5 g. of  $\beta$ -naphthoquinoline in a mixture of 1.3 ml. of concentrated sulfuric acid and 3 ml. of water, and dilute with water to 100 ml.

**Wash solution.** Dilute 10 ml. of the 2.5 per cent solution of  $\beta$ -naphthoquinoline to 90 ml. with water, and add 10 ml. of 0.2 N potassium iodide solution.

**Procedure.** To a neutral solution containing only cadmium, add 50 ml. of 2 N sulfuric acid and 50 ml. of a 10 per cent sodium tartrate solution. Then add a slight excess of the 2.5 per cent  $\beta$ -naphthoquinoline solution and a little sulfurous acid, and finally dilute to 150 ml. Add a slight excess of 0.2 N potassium iodide solution and allow the mixture to stand 15-20 minutes. Filter off the white crystalline precipitate of the cadmium compound. Wash free of acid with the wash solution. Suck dry, and decompose the precipitate by heating with 20 ml. of 2 N sodium hydroxide solution. Acidify slightly with hydrochloric or sulfuric acid, and make the acid concentration about 5 per cent. Titrate the solution by the cyanide method of Lang,<sup>10</sup> or by the iodine-acetone method of Berg.<sup>11</sup>

The cyanide determination is based on the following reaction:



Carry out the titration as follows: The volume of the iodide solution should be at least 50 ml., and to this add an equal volume of 2-5 N hydrochloric acid or 4-5 N sulfuric acid. Then add 6-8 ml. of 0.5 N potassium cyanide and a little starch. Titrate with 0.025 M potassium iodate solution to the disappearance of the blue color. One ml. of 0.025 M  $KIO_3$  = 1.405 mg. of cadmium.

According to the iodine-acetone method, hydrogen iodide is oxidized to iodine with iodate in the presence of acetone.



This determination is carried out as follows: Dilute the iodide solution to a volume of 50-60 ml. with water, and add 20-30 ml. of acetone. Adjust the acidity of the mixture to 2-2.5 N with a 50 per cent sulfuric acid solution. The total



volume should be about 100 ml. Add a little starch solution, and titrate with 0.1 N potassium iodate solution. The titration should be carried out at such rate that the starch-iodine color remains its normal blue and does not become dirty brown. Titrate to the disappearance of the blue color. One ml. of 0.1 N  $\text{KIO}_3$  = 0.9366 mg. of cadmium.

The above method is suitable for the separation of zinc and cadmium. Cadmium is precipitated as described above and zinc is determined in the filtrate.

Pass and Ward<sup>3</sup> have recommended the following procedure for determining cadmium in the presence of other metals of the second analytical group:

**Procedure.** To 50 ml. of the solution to be analyzed, which is 2 N in sulfuric acid, add a few drops of sulfurous acid and heat to boiling, add a few pieces of bright iron and continue to boil the solution for a time. Replace the water that is lost by evaporation. Keep the mixture at a temperature just below the boiling point for 1 hour. Filter through a sintered glass crucible containing a piece of iron wire to remove lead sulfate and the metals which have been precipitated by treating with iron. Wash the residue with cold water and add the washings to the original filtrate.

To the filtrate, which should have a volume of 100-120 ml., add 5 ml. of Rochelle salt, a few drops of sulfurous acid and 40-50 ml. of 0.2 N potassium iodide solution. Add sufficient 2.5 per cent  $\beta$ -naphthoquinoline in 0.2 N sulfuric acid to precipitate cadmium and to provide an excess of 5-6 ml. in a total volume of 140-150 ml. Allow the mixture to stand for 1 hour and filter. Wash the precipitate thoroughly with a mixture of 10 ml. of 0.2 N potassium iodide, 10 ml. of the reagent solution, and a few drops of sulfurous acid. Remove most of the adhering liquid with suction, and transfer the precipitate to the beaker in which the original precipitation was carried out.

Titrate the precipitate with 20 ml. of 2 N ammonium hydroxide and filter. Wash the precipitate thoroughly with 2 N ammonium hydroxide and water. Transfer the filtrate to a long-necked flask, and rinse the flask with 2 N hydrochloric acid. Use about 100 ml. of the acid so that the solution will be about N in hydrochloric acid at the completion of the final titration. Then add 5 ml. of 10 per cent potassium cyanide and a little starch solution, and titrate with 0.025 M potassium iodate solution until the blue color which first develops changes to a reddish-violet and finally disappears. One ml. of the potassium iodate solution = 1.405 mg. of cadmium.

Not more than 50 mg. of cadmium can be determined by this procedure.

Kiba and Sato<sup>4</sup> have studied the possibility of weighing the cadmium precipitate as  $(\text{C}_{13}\text{H}_9\text{N})_2 \cdot \text{H}_2(\text{CdI}_4)$ , and recommend 110-130° C. as the proper temperature for drying the precipitate.

**Detection of zinc.**  $\beta$ -Naphthoquinoline reacts with zinc in the presence of a thiocyanate and in an acid solution to form a colorless, crystalline compound which may be used for the detection of zinc.<sup>5</sup> This compound probably corresponds in composition to  $(\text{C}_{13}\text{H}_9\text{N})_2 \cdot \text{H}_2\text{Zn}(\text{CNS})_4$ . The test is carried out as follows:

**Reagent.** Add a 5-10 per cent aqueous solution of potassium thiocyanate to a 1 per cent solution of  $\beta$ -naphthoquinoline in 0.1 N sulfuric acid until a slight permanent turbidity is obtained. Approximately 0.15 ml. of 10 per cent potassium thiocyanate is required for 1 ml. of the reagent solution.

**Procedure.** When the above reagent is added to a neutral or slightly acid solution containing zinc, a very finely divided precipitate is formed, which at first apparently consists of tiny droplets, but which eventually develops into thin colorless crystals. In the presence of 2 N sulfuric acid, characteristic crystals are obtained at zinc concentrations as low as 1:200,000.

The above test may be carried out in the presence of moderate quantities of barium, calcium, magnesium, beryllium, aluminum, chromium, cerium, lead, arsenic, manganese, nickel and the alkali metals. Acetic acid should be substituted for sulfuric acid when lead or barium is present. Cadmium, in concentrations below 0.5 per cent, does not interfere. Ferric iron in concentrations up to 1 per cent does not interfere if the test is carried out in a 50 per cent phosphoric acid solution. Most of the other metals give precipitates with  $\beta$ -naphthoquinoline.

**Determination of tungsten.** Platonov and Kirillova<sup>6</sup> have found that  $\beta$ -naphthoquinoline can be used to replace cinchonine in the quantitative precipitation of tungstic acid.

**Determination of germanium.**  $\beta$ -Naphthoquinoline forms with trioxalatogermanic acid,  $\text{H}_2\text{Ge}(\text{C}_2\text{O}_4)_3$ , and insoluble derivative which appears promising as a precipitation form for the determination of germanium.<sup>9</sup> The precipitation procedure is simple, and yields a product of very high molecular weight. The precipitate is crystalline and easy to filter and wash. It is readily converted to germanium dioxide.

**Reagent.** Treat 10 g. of  $\beta$ -naphthaquinoline with 5 g. of oxalic acid dissolved in 50 ml. of water. Heat to promote solution of the base, and filter while still hot. Dilute with water to 500 ml.

**Procedure.** Dilute the solution containing 50-75 mg. of  $\text{GeO}_2$  to 400 ml. and add 5 g. of oxalic acid. Heat to promote the formation of the trioxalatogermanic acid. Add 25 ml. of the  $\beta$ -naphthoquinoline solution, and allow the mixture to cool to room temperature. Allow to stand overnight and filter. Wash the precipitate with a dilute solution of oxalic acid and the reagent. Ignite in a platinum crucible in a muffle at 700-800° C. Weigh as  $\text{GeO}_2$ .

All elements which form insoluble oxalates when treated with oxalic acid interfere and must be removed. Titanium, tin, and zirconium, and to a lesser extent, iron, form complex oxalates which are precipitated by  $\beta$ -naphthoquinoline.

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**NITROQUINETOL**

Synonym: 5-Nitro-6-ethoxyquinoline

 $C_{11}H_{10}O_3N_2$ 

Mol. Wt. 218.19

Beil. Ref. XXI, 90.

**Use:** Detection and determination of nitrate.

Nitroquinetol is a crystalline solid melting at 110-111° C. It is very slightly soluble in water but dissolves in about 20 parts of alcohol.

**Preparation:** Dissolve 1 mole of quinetol (6-ethoxyquinoline) in sulfuric acid and add 2 moles of fuming nitric acid. On pouring this liquid into ice water, a precipitate of nitroquinetol nitrate is obtained.

The nitro derivative is isolated by suspending the nitrate in water and decomposing with an excess of sodium or potassium hydroxide. It is possible to obtain nitroquinetol directly by adding quinetol nitrate to sulfuric acid and precipitating with ammonium hydroxide after diluting the mixture with water. Purify the reagent by recrystallizing from 5 or 6 parts of boiling alcohol.

**Detection and determination of nitrate.** Nitroquinetol is only slightly basic, but forms salts with the strong mineral acids. The nitrate is almost completely insoluble in cold water, and its formation from nitroquinetol can be used for the detection and determination of nitric acid and nitrates. A solution of 2 g. of nitroquinetol in 3 parts of sulfuric acid and 60 parts of water yields a precipitate immediately upon the addition of a few drops of a 0.2 per cent solution of nitric acid or of a nitrate.

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**6-NITROQUINOLINE** $C_9H_6O_2N_2$ 

Mol. Wt. 174.15

Beil. Ref. XX, 372.

**Use:** Determination of palladium.

6-Nitroquinoline crystallizes in colorless needles which melt at 150-151° C. It is very slightly soluble in water, ethyl alcohol and ether.

**Preparation:** Dehydrate about 75 g. of glycerol by heating in an open dish to 150° C., and also dehydrate about 35 g. of arsenic acid by heating to 110-120° C. in an air-oven for several hours with stirring. Now mix 28 g. of *p*-nitroaniline, 60 g. of anhydrous glycerol and 55 g. of concentrated sulfuric acid and

allow to cool, and then add 29 g. of the anhydrous arsenic acid. Heat the mixture gently with reflux on a sand-bath until bubbles appear to rise through the liquid. Then remove the flame until the initial reaction is over, and then continue the gentle boiling for 2 or 3 hours. Cool the mixture and dilute with twice its volume of water and allow to stand for several hours. Filter, and carefully neutralize with a solution of sodium hydroxide, avoiding any marked increase in temperature. Filter off the gray precipitate of 6-nitroquinoline. Wash with water, and dissolve in dilute hydrochloric acid. Boil the resulting solution for several hours with a little animal charcoal and filter while hot. Allow the filtrate to cool and again neutralize with sodium hydroxide. Filter off the precipitate, wash well, and dry. Dissolve in a little alcohol containing animal charcoal. Filter, and collect the crystals which are obtained upon cooling. The yield may be increased by further evaporating the alcoholic solution.<sup>1</sup>

**Determination of palladium.** A flocculent precipitate is formed when a solution of a palladium salt is treated with a hot saturated solution of 6-nitroquinoline. Since precipitation is quantitative, this reaction may be used for the gravimetric determination of palladium.<sup>2</sup> The precipitate may be washed and weighed as  $\text{Pd}(\text{C}_9\text{H}_6\text{N}-\text{NO}_2)_2$ , or it may be ignited in hydrogen and weighed as metallic palladium.

**Procedure.** Heat the solution to be analyzed to boiling and add a hot saturated solution of 6-nitroquinoline. Stir well and boil the mixture for 5 minutes. Allow to stand for 15-20 minutes and filter off the thick flocculent yellow precipitate. Wash with distilled water until free of chlorides. Dry, ignite carefully in air, and for 30 minutes at a red heat in a stream of hydrogen. Cool and weigh as metallic palladium. The precipitate may be dried and weighed as  $\text{Pd}(\text{C}_9\text{H}_6\text{N}-\text{NO}_2)_2$ . The factor is 0.2345. Platinum does not interfere with this procedure.

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## 8-NITROQUINOLINE

Synonym: *o*-Nitroquinoline



Mol. Wt. 174.15

Beil. Ref. XX, 373.



**Use:** Determination of bismuth.

8-Nitroquinoline is a crystalline solid melting at 91-92° C. It is almost insoluble in cold water, but is moderately soluble in alcohol and ether and dissolves readily in benzene.

**Preparation:** Mix 51.5 g. of arsenic acid, 100 g. of concentrated sulfuric acid, 110 g. of glycerol and 50 g. of *o*-nitroaniline and heat carefully on a sand-bath to the first appearance of a reaction. Remove the mixture from the steam bath and keep the liquid at a gentle boil for about 3 hours. Dilute the mixture strongly with water, allow to stand for a short time, and filter off the brown

precipitate. Carefully add sodium hydroxide until the reaction is alkaline and again filter at the first turbidity. The reagent separates as soon as the excess acid is neutralized as a brown flocculent mass. Allow to stand for 1 hour, filter, and purify by heating the alcoholic solution with animal charcoal. Again filter, mix with water, and filter off the crystalline precipitate.<sup>1</sup>

**Determination of bismuth.** Canneri and Bigalli<sup>2</sup> have substituted 8-nitroquinoline for 8-hydroxyquinoline, and naphthoquinoline, which have been used for the determination of bismuth as the iodo-salts. The gravimetric method has not proved very satisfactory, since it is very difficult to ignite and wash the precipitate properly, and the residue is hygroscopic. A volumetric method is more satisfactory. Bismuth is precipitated as usual, the precipitate filtered off, and the residue dissolved in 10 per cent hydrochloric acid. Berg<sup>3</sup> titrated the organic molecule with iodine in the presence of acetone with potassium iodate, but Canneri and Bigalli obtained good results by titrating the liberated iodine with nitrous acid or by extracting the iodine with carbon disulfide and titrating with sodium thiosulfate.

Antimony and tin give similar precipitates with the quinoline derivatives, and must be absent while making the bismuth determination. Oxidizing agents and metals whose iodides are insoluble also interfere.

1. C. A. Knueppel, *Ber.* 29, 705 (1896).

2. G. Canneri and D. Bigalli, *Ann. chim. appl.* 26, 455-60 (1936); *C.A.* 31, 2545 (1937).

3. R. Berg and O. Wurm, *Ber.* 60, 1664-71 (1927).

## QUINALDINE

Synonym: 2-Methylquinoline,  $\alpha$ -methylquinoline

$C_{10}H_9N$

Mol. Wt. 143.18

Beil. Ref. XX 388.

$C_9H_8N-CH_3$

**Use:** Determination of bismuth.

Quinaldine is a colorless, oily liquid, which possesses a quinoline odor. On exposure to air, the liquid turns reddish-brown in color. It has a sp. gr. of 1.186 and boils at 246-247° C. The compound is insoluble in water, but soluble in ether and chloroform. It should be stored in a tightly closed container, and well protected from light.

**Preparation:** Add gradually 80 parts of paraldehyde to a cooled mixture of 40 parts of aniline, 45 parts of nitrobenzene and 100 parts of concentrated sulfuric acid, and heat 4-5 hours on a sand bath to gentle boiling. Dilute the mixture with water and steam distill the unchanged nitrobenzene. Separate the crude base with sodium hydroxide, and again distill with steam. Purify by distillation. The fraction boiling at 246-248° C. is quinaldine.<sup>1</sup>

Quinadine may also be prepared as follows: To a mixture of 30 g. of concentrated hydrochloric acid and 10 g. of zinc chloride, add 15 g. of aniline, and reflux the mixture on a water bath. Add slowly during a period of 2 hours 12.5 g. of acetaldehyde. Boil on a sand bath for 90 minutes. Make alkaline with sodium hydroxide and steam distill. Separate the crude quinaldine and distill. Collect the fraction boiling at 244-250° C.<sup>2</sup>

**Determination of bismuth.** Bismuth may be determined in the presence of a number of other ions by the following procedure: <sup>3</sup>

**Reagents.** *Quinaldine-potassium iodide solution:* Dissolve 150 ml. of quinaldine, 50 ml. of concentrated sulfuric acid, and 75 g. of potassium iodide in water and dilute to 1 liter.

*Quinaldine wash liquid:* Dissolve 35 ml. of quinaldine, 15 ml. of concentrated sulfuric acid, and 0.8 g. of potassium iodide in water and dilute to one liter.

**Procedure.** Dissolve the material to be analyzed, containing about 0.03 g. of bismuth, in sulfuric acid and dilute the resulting solution to 200 ml. Adjust the acidity to approximately 1.0 N. Add 15 ml. of 10 per cent sodium sulfite, and precipitate bismuth by adding dropwise the quinaldine-potassium iodide reagent. Allow to stand 20 minutes with occasional stirring and filter. Wash the red precipitate with 40-50 ml. of the quinaldine wash liquid, and finally with 30 per cent acetone in dibutyl ether.

Dissolve the precipitate in 100 ml. of 5 per cent sodium hydroxide and heat almost to boiling for about 20 minutes to insure complete decomposition. Cool, neutralize with hydrochloric acid, and add 10 ml. of concentrated hydrochloric acid. Finally, add 8 ml. of 0.5 M potassium cyanide solution and titrate with potassium iodate to ICN.<sup>4</sup>



One ml. of 0.025 M KIO<sub>3</sub> = 0.06345 g. I<sup>-</sup> or 2.612 mg. bismuth.

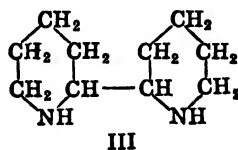
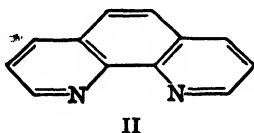
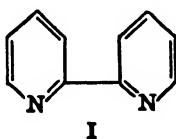
The above procedure can be used for determining as little as 0.3 mg. of bismuth in the presence of lead, antimony, tin, cadmium, copper, iron, chromium, manganese, cobalt, calcium, barium, uranium, nickel, beryllium, aluminum, titanium, zinc, sodium, potassium, arsenic and phosphate. Silver, mercury and large quantities of chloride interfere and must be removed.

1. O. Doebner and W. v. Miller, *Ber.* **14**, 2812, 2816 (1881).
2. O. Doebner and W. v. Miller, *Ber.* **16**, 2465 (1883).
3. J. R. Hayes and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.* **11**, 531-2 (1939); *C.A.* **33**, 9186 (1939).
4. R. Lang, *Z. anorg. allgem. Chem.* **122**, 332-48 (1922); *C.A.* **16**, 3824 (1922).

## CHAPTER III

### DIPYRIDYL AND RELATED COMPOUNDS

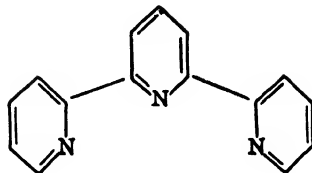
In a classic paper on complexes, Blau<sup>1</sup> reported that 2,2'-dipyridyl (I), 1,10-phenanthroline (II) and 2,2'-dipiperidyl (III) form water-soluble, intensely red ferrous salts, which are stable toward acids. The color is caused by the formation of complex ions, such as  $[\text{Fe}(\text{dipy})_3]^{+2}$  and  $[\text{Fe}(\text{phen})_3]^{+2}$ . These ions belong to the class of the hexammines, since the 6 coordination positions of each iron atom are occupied by 3 molecules of the base, each of which contains 2 nitrogen atoms.



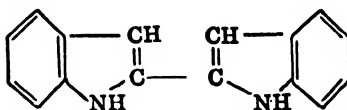
One of the remarkable properties of these ferrous salts is their extraordinary stability. They are not readily oxidized to the corresponding ferric compounds, and are stable in the presence of alkali hydroxides and alkali sulfides. This stability is attributed to the formation of 5-membered rings in the complex ions. It is an interesting fact that the ferric dipyridyl or ferric phenanthroline ion cannot be prepared from ferric salts and the corresponding bases, but only by the oxidation of the ferrous complexes with potassium permanganate in an acid solution. Once formed, however, the ferric complexes are reduced to the ferrous compounds, even by the weakest reducing agents. Thus, in the ferrous dipyridyl and ferrous phenanthroline complexes there is a complete reversal of the stability relationship usually exhibited by the non-complex, soluble ferric and ferrous salts.

2,2'-Dipyridyl and 1,10-phenanthroline are used in analytical chemistry for the detection and colorimetric determination of ferrous iron, since these reagents appear to be specific for the ferrous ion. These reactions may also be used indirectly in the analysis of ferric iron, since the latter is easily reduced to the ferrous state.

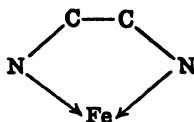
The reactions of 2,2'-dipyridyl, 1,10-phenanthroline and dipiperidyl, as well as those of 2,2',2''-terpyridyl, which react similarly, indicate clearly that the grouping  $-\text{N}-\text{C}-\text{C}-\text{N}-$  is responsible for the formation of the red complex with ferrous ions. It is further apparent that this grouping alone is not sufficient, since the characteristic ferrous reaction is not given by ethylenediamine,  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ . The molecule containing the reactive grouping must contain the structure of 2,2'-dipyridyl.



and 2,2'-biindoyl



Smirnoff <sup>2</sup> and Willink and Wibaut <sup>3</sup> have studied the properties of a number of derivatives of 2,2'-dipyridyl in an effort to determine the effect of other groups upon the ferrous iron reaction. The compounds investigated were 2-pyridyl-2-quinoline, 2,2'-biquinolyl, 3,3'-dicarboxy-2,2'-dipyridyl, 6,6'-dimethyl-2,2'-dipyridyl and 6,6'-diamino-2,2'-dipyridyl. It is an interesting fact that these compounds, although they contain the iron-specific group, do not react with ferrous salts. According to Smirnoff,<sup>2</sup> quinolyl pyridine, and diquinolyl do not form ferrous complexes because the nitrogen is no longer capable of forming a coordinate bond, due to the fact that there is a system of conjugated double bonds adjacent to one or both of the nitrogen atoms. This assumption is supported by the fact that quinoline has a lower basicity and a smaller capacity for addition than pyridine. This difference in behavior is attributed to the fact that the ability of the nitrogen atom in quinoline to form an auxiliary valence bond is reduced by the spatial proximity of the conjugated double bonds of the benzene ring, while in pyridine, which is completely symmetrical, there is no such interference. These considerations, however, cannot be applied to the dicarboxyl, dimethyl or diamino derivatives of dipyridyl. In these substances, then, it must be assumed that the configuration of the two pyridine rings is different from that in 2,2'-dipyridyl from which they are derived. For example, an examination of the structural formula of the ferrous dipyridyl complex reveals that the iron atom forms, with each dipyridyl molecule, a 5-membered ring of the type



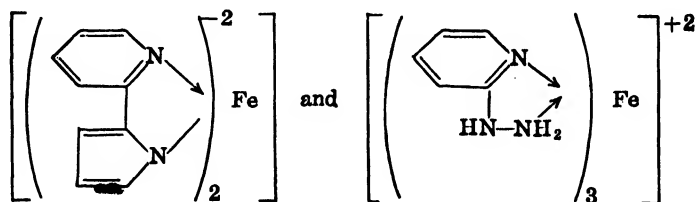
Each of these rings is undoubtedly planar. In 2,2'-dipyridyl the —N—C—C—N— system can assume a planar arrangement because of the free rotation of the pyridine rings about the 2,2'-bond. In 3,3'-(2,2')-dipyridyldicarboxylic acid the —N—C—C—N— grouping cannot lie in one plane because of restricted rotation due to the steric interference of the carboxyl groups.<sup>4</sup>

From the above discussion it will be seen that the presence of the specific atomic grouping, —N—C—C—N—, alone is not sufficient to confer upon the



molecule in which it is contained the characteristic iron reaction, but, in addition, the influence of the substituent groups must be favorable.

An understanding of the relationship of atomic grouping to the ferrous iron reaction is further complicated by the fact that 2-(2'-pyridyl)pyrrole and 2-pyridylhydrazine, which are structurally similar to 2,2'-dipyridyl, also form complex salts or ions, namely



but in contrast to the complex salts with dipyridyl and phenanthroline, these are very unstable, and are immediately oxidized by air to the corresponding ferric salts.<sup>5-7</sup>

Some of the salts of ferrous dipyridyl and ferrous phenanthroline are insoluble in water. For example, red precipitates are obtained when  $\text{Na}_2[\text{Ni}(\text{CN})_4]$  or  $\text{K}_2[\text{HgI}_4]$  are added to solutions containing the  $[\text{Fe}(\text{dipy})_3]^{+2}$  ion. The formation of these precipitates may provide a suitable means for determining small quantities of mercury, nickel or iron.<sup>8</sup> The perchlorate, periodate and persulfate of the ferrous phenanthroline complex are only slightly soluble in water.

Tartarini<sup>9</sup> has prepared a number of insoluble, colored complex compounds of the cuprous halides and thiocyanate with 2,2'-dipyridyl and 1,10-phenanthroline. Among these are the red  $\text{CuI} \cdot (\text{dipy})$ , orange  $\text{CuSCN} \cdot (\text{dipy})$ , yellow-brown  $\text{CuSCN} \cdot (\text{phen})$  and blue  $\text{CuI} \cdot (\text{phen})$ .

Komarovsky and Poluektov<sup>10</sup> report that reduced molybdenum produces with 2,2'-dipyridyl a water-soluble, red compound of unknown composition.

Phenanthroline and the substituted phenanthrolines and their ferrous complexes, as well as those with dipyridyl and terpyridyl, may be used as precipitants for a number of ions. There is the possibility that many important analytical procedures may be based on this principle. The details of such reactions as have been studied are included in the separate sections on each of above reagents.

Since many of the analytical uses of dipyridyl and 1,10-phenanthroline and substituted 1,10-phenanthrolines require 0.01 or 0.025 N solution of their ferrous complexes, the data for preparing these solutions are given in Table 8. This information is taken from the booklet on "Phenanthroline and Substituted Phenanthroline Indicators" by Smith and Richter.<sup>4</sup>

1. F. Blau, *Monatsh.* **19**, 647 (1898).
2. A. Smirnoff, *Helv. Chim. Acta.* **4**, 802 (1921).
3. H. T. Willink, Jr., and J. Wibaut, *Rec. trav. chim.* **54**, 275 (1935).
4. A. F. Smith and F. P. Richter, *Phenanthroline and Substituted Phenanthroline Indicators* (booklet), The G. Frederick Smith Co., Columbus, Ohio.
5. B. Emmert, *Ber.* **60**, 2211 (1927).

TABLE 8.—PREPARATION OF SOLUTIONS OF THE FERROUS COMPLEXES OF 2,2'-DIPYRIDYL, 1,10-PHENANTHROLINE, 5-METHYL-1,10-PHENANTHROLINE AND 5-NITRO-1,10-PHENANTHROLINE

Organic Base	Formula	Mol. Wt.	Organic Base Required in g.		FeSO <sub>4</sub> ·7H <sub>2</sub> O Required in g.		Dilute with H <sub>2</sub> O to
			0.01 N	0.025 N	0.01 N	0.025 N	
Dipyridyl	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	156.18	4.6854	11.7135	2.7802	6.9505	1000 ml.
1,10-Phenanthroline	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> ·H <sub>2</sub> O	198.216	5.9465	14.8662	2.7802	6.9505	1000 ml.
5-Methyl-1,10-phenanthroline	C <sub>13</sub> H <sub>7</sub> N <sub>2</sub> CH <sub>3</sub>	194.226	5.8268	14.5670	2.7802	6.9505	1000 ml.
5-Nitro-1,10-phenanthroline	C <sub>12</sub> H <sub>7</sub> N <sub>2</sub> NO <sub>2</sub>	225.20	6.7560	16.8900	2.7802	6.9505	1000 ml.

6. B. Emmert, *Ber.* 62, 1733 (1929).
7. B. Emmert, *Ber.* 66, 1871 (1933).
8. F. Feigl, *Specific and Special Reactions*, p. 116, Elsevier-Nordeman, New York (1940).
9. G. Tartarini, *Gazz. chim. ital.* 63, 597 (1933).
10. K. Komarovskiy and N. Poluektov, *Mikrochim. Acta.* 1, 264 (1937).

**2,2-BIQUINOLYL**

Synonym: 2-[2-Quinolyl]-quinoline

 $C_{18}H_{12}N_2$ 

Mol. Wt. 256.28

 $C_9H_6N-C_9H_6N$ **Use:** Detection and determination of copper.

2,2-Biquinolyl occurs as glistening leaves. It melts at 196° C. The free base is insoluble in water, but is somewhat more soluble in organic solvents.

**Preparation:** Mix 2.42 g. of *o*-aminobenzaldehyde and 3.46 g. of 2-quinolylmethyl ketone in 50 ml. of alcohol, and add 5 ml. of N potassium hydroxide. Heat the mixture under reflux for one hour on a water bath. Recrystallize with animal charcoal, filter, and dilute with water until a turbidity appears. The base is obtained as a crystalline solid.<sup>1</sup> *o*-Aminobenzaldehyde is prepared according to the method of Bamberger and Demuth,<sup>2</sup> and 2-quinolylmethyl ketone is prepared according to the method of Kaufmann and Burkhardt.<sup>3</sup>

**Detection and determination of copper.** 2,2-Biquinolyl reacts with solutions of cuprous ions under certain conditions to give a purple color. The intensity of the color produced is in agreement with Beer's law. A method for the detection and determination of copper has been based upon this reaction.<sup>4</sup> The sensitivity of this reaction is 1 part of copper in 100,000,000 of solution.

Stable complexes with cupric and cobalt ions have also been prepared. 2,2-Biquinolyl base reacts with cupric chloride to give orange-red crystals (m.p. = 338° C.) corresponding to the formula,  $C_{18}H_{12}N_2 \cdot CuCl_2$ . The reagent also reacts with copper sulfate to give a green crystalline compound, and with cobalt chloride to give a grass-green crystalline precipitate (m.p. = 360° C.) corresponding to the formula,  $C_{18}H_{12}N_2CoCl_2$ . The brownish-green crystals of  $(C_{18}H_{12}N_2)_2 \cdot CuCl$ , which decompose above 195° C., and which are insoluble in water and benzene, are prepared by the action of 2,2-biquinolyl base on cuprous chloride.

1. A. P. Smirnoff, *Helv. Chim. Acta.* 4, 802-11 (1921); *C.A.* 16, 234 (1922).
2. E. Bamberger and O. Demuth, *Ber.* 34, 1329 (1901).
3. A. Kaufmann and H. Burkhardt, *Ber.* 46, 2931 (1913).
4. J. G. Breckenridge, R. W. J. Lewis, and L. A. Quick, *Can. J. Research.* 17B, 258-65 (1939); *C.A.* 33, 9184 (1939).

**2,2'-DIPYRIDYL**Synonym:  $\alpha, \alpha'$ -Dipyridyl $C_{10}H_8N_2$ 

Mol. Wt. 156.18

Beil. Ref. XXIII, 199.

 $C_5H_4N-C_5H_4N$

**Use:** Detection of cadmium, columbium, copper, dichromate, ferricyanide, iron, ferrocyanide, molybdenum, permanganate, platinum, rhenium, tantalum, thiocyanate, tin and vanadate.

Determination of cadmium and iron.

2,2'-Dipyridyl is a white crystalline solid. It melts at 69-70° C. and boils at 272-273° C. It dissolves in about 200 parts of water, but is very soluble in alcohol, ether, benzene and chloroform.

**Preparation:** The preparation of 2,2'-dipyridyl was first described by Blau,<sup>2</sup> and was later prepared by methods of hydrogenation by Meyer and Hoffman-Meyer,<sup>49</sup> by Hein and co-workers,<sup>1,50</sup> and by Wibaut and Willink.<sup>51</sup> Hein and Retter<sup>1</sup> have described a method based on the dehydrogenation of pyridine with anhydrous ferric chloride.

**Preparation:** Dry 70 g. of pyridine over sodium hydroxide, and mix with 13 g. of anhydrous sublimed ferric chloride. Heat to 300° C. for about 35 hours in a sealed tube. At first the mixture is brown in color, but later becomes black, and on cooling solidifies to a mass of red-black crystals, which is surrounded by a deep red liquid. Open the tube and wash out the reaction product with a little hot water. This yields an opaque, red-black solution. Rapidly extract the liquid with a little ether to remove any oily impurities, neutralize with sodium bicarbonate, and then heat with steam to remove the excess pyridine. Make the mixture strongly alkaline, and finally distill 2,2'-dipyridyl with steam until the distillate gives only a slight reddish coloration when treated with a solution of ferrous ammonium sulfate. Acidify the distillates and concentrate by evaporation. Add sodium hydroxide and extract with ether. Dry the ether extract over sodium sulfate and remove the ether by evaporation *in vacuo* over concentrated sulfuric acid. An impure product consisting of brown crystals is obtained. Purify by dissolving in ether and shaking three times with animal charcoal. The filtrate should then be colorless and yield white, leaf-like crystals upon evaporation. Again crystallize from dilute alcohol.<sup>1-3,12,24</sup>

Morgan and Burstall<sup>3</sup> have applied the method of Hein and Retter<sup>1</sup> to the preparation of the dipyridyls, terpyridyls, and other compounds. In this process, 8,000 g. of pyridine and 1,524 g. of anhydrous ferric chloride were placed in an iron autoclave fitted with a mechanical stirrer and lined with stainless steel, and then allowed to react 36 hours at a temperature of 500° C. and a pressure of 50 atmospheres. The principal product consisted of the isomeric dipyridyls and at least 20 other products. The products are classified as follows:

1. Small quantities of gases consisting of hydrogen, nitrogen, ammonia, saturated hydrocarbons and ethylene.
2. A nitrogenous neutral oil boiling at 90-130° C.
3. A fraction consisting of pyridine and the mono- and dimethyl, ethyl and propyl derivatives of pyridine.
4. Dipyridyls and dipiperidyls, including the 2,2'-, 3,4'-, 2,3'-, and 2,4'-isomers. This fraction contains approximately 524 g. of 2,2'-dipyridyl. Certain

dialkylated derivatives of this compound are also present. All the members of this group are volatile with steam from an alkaline solution.

5. The terpyridyls are not volatile with steam from an alkaline solution, and are recovered from the residue after steam distillation of the compounds of Group 4 by treating with a large excess of sodium hydroxide and extracting with benzene. 55 g. of 2,2',2''-terpyridyl is obtained in this way. Other 2,2',X''-terpyridyls are formed.

6. Resinamines.

7. Insoluble residue.

A summary of the products of the reaction of Morgan and Burstall is given as follows:

Pyridine Used g.	Anhyd. FeCl <sub>3</sub> g.	Pyridine Recovered g.	Alkylated Pyridines g.	Dipyridyls g.	Terpyridyls g.	Resinamines g.
8000	1524	5630	245	794	225	512

The properties and physical constants of the isomeric dipyridyls, which are taken from the work of Smith,<sup>51</sup> are shown in Table 9.

TABLE 9.—PROPERTIES OF THE ISOMERIC DIPYRIDYLS

Isomer	M.P. ° C.	B.P. ° C.	M.P. of Picrate ° C.	Solubility in Water
2,2'-dipyridyl	69.5	272.5	158	Only slightly
2,3'-dipyridyl	Liquid	287-289	149.5	Insoluble
3,3'-dipyridyl	68	291-292	232	All proportions
4,4'-dipyridyl	114	305	213	Sol. in hot water
3,4'-dipyridyl	61	297	215	V. sol. cold water
2,4'-dipyridyl	Liquid	280-282	208	Sl. sol. in hot water

Hill<sup>11</sup> has used the following method: Dissolve 173 g. of potassium permanganate in 4,250 ml. of water and mix with 45 g. of  $\alpha$ -picoline (B.P. 126-132° C.), and heat under reflux for 7 hours. Filter and reduce the alkalinity of the filtrate by adding a stream of carbon dioxide. Distill the greater part of the water and unchanged base, and evaporate the residual liquid to dryness on a water bath. Dissolve the residue in 150 ml. of water and filter. Add glacial acetic acid until the pH is 5-6, and then add about 180 ml. of 1 per cent copper sulfate solution slowly until precipitation is complete. Allow to stand 15 minutes and filter off the copper salt of picolinic acid. Wash with cold water and dry, first at room temperature, and then at 105° C. Destructively distill dry copper picolinate in a slow current of carbon dioxide from a retort until only

a black residue remains. The receiver is cooled in ice. The liquid distillate contains 2,2'-pyridyl and pyridine. Heat this liquid to 50° C. on a water bath and remove most of the pyridine with a current of air. Cool the residue, add a few drops of 40 per cent soda solution and distill with steam. Continue the distillation until the distillate gives only a faint color with ferrous sulfate. Evaporate to dryness with an excess of hydrochloric acid on a water bath. Dissolve in a little water, make alkaline with a little soda and again distill with steam. The reagent is obtained as shining plates.

Two new procedures have been proposed for the preparation of 2,2'-dipyridyl, which may offer some advantages over those described above. The following descriptions of these methods are taken directly from the work of Smith and Richter.<sup>39</sup>

**The Grignard reaction in the synthesis of dipyridyl from 2-bromopyridine.** By this procedure, the best of several modifications, 2-bromopyridine and cobaltous chloride are caused to react with ethyl magnesium bromide.

**Experimental procedure.** The entire Grignard reaction, consisting of two parts, the preparation of the Grignard reagent and the coupling reaction, was carried out in a 3-necked flask fitted with a separatory funnel in one arm, a sealed stirrer in the center, and a reflux condenser and drying tube in the remaining opening. Provision was made for the application of external heat using an electric cone heater controlled by use of a variac.

**Preparation of ethyl magnesium bromide.** Three grams of magnesium (0.1 mole for ethyl bromide, plus excess) was placed in the reaction flask. To this was added a few milligrams of iodine crystals. Through the separatory funnel was added 10.9 g. (0.1 mole) of ethyl bromide. After the vigorous initial reaction had subsided, the mixture was boiled gently on the heating cone for 15 minutes. Ethyl bromide was then added to react with any excess magnesium metal which remained.

**Reaction of ethyl magnesium bromide with 2-bromopyridine in the presence of cobaltous chloride.** To the cooled reaction mixture from the ethyl magnesium bromide preparation, a mixture of 16 g. (0.1 mole) of 2-bromopyridine and 1.3 g. (0.01 mole) of anhydrous cobaltous chloride in dry ether was added at such a rate as to obtain moderate refluxing of the ether. After the initial reaction was finished, the mixture was heated for two hours. The final isolation of 2,2'-bipyridyl was then carried out. By transferring the reaction ingredients to a steam distillation apparatus, acidifying with hydrochloric acid and applying steam, the organic products other than the bipyridyl were removed. The reaction mixture was then made alkaline using caustic soda and again steam distilled until the distillate no longer gave a test with ferrous ion. A small excess of hydrochloric acid was added to the distillate to prevent loss of bipyridyl by volatilization and the volume diminished by evaporation. After the addition of caustic soda, the bipyridyl was extracted using ether and the product isolated by evaporation of the ether solution. The final product (1.5 g. or 19 per cent of theory) had a melting point of 70° C.

The second method uses 1,10-phenanthroline as the starting material.

**The preparation of 3,3'-dicarboxy-2,2'-dipyridyl from 1,10-phenanthroline.** The quantities of materials employed in molecular ratio were as follows:

- 1 mole of 1,10-phenanthroline monohydrate
- 3 moles of potassium permanganate (one-third mole excess)
- 2 moles of sodium hydroxide
- 2 moles of silver nitrate

Following these proportions, 8 g. (0.04 mole) of 1,10-phenanthroline was suspended in 800 ml. of water; 3.2 g. (0.08 mole) of sodium hydroxide was added; 19 g. (0.12 mole) of potassium permanganate was slowly added in the form of its crystals. After fifteen minutes the solution was heated to boiling and kept at this temperature for two hours. Throughout the entire operation the mixture was thoroughly agitated using a mechanical stirrer. Finally the excess permanganate was reduced by adding sucrose until no further permanganate color remained as tested by applying a drop of the reaction mixture to an area of filter paper and examining the spot test fringe for a purple border.

The voluminous precipitate of manganese dioxide was filtered out and the filtrate concentrated on the steam bath. The concentrate was acidified, using acetic acid and the carbon dioxide thus evolved was displaced from solution by stirring and digestion; 13.6 (0.08 mole) of silver nitrate was dissolved in the minimum required quantity of water added slowly with constant stirring. The resulting precipitate was filtered and transferred to a considerable volume of hot water in a precipitation flask and saturated with hydrogen sulfide. The silver sulfide was filtered and the filtrate treated with norite decolorizing carbon. After boiling to expel hydrogen sulfide the solution was filtered and the resulting colorless solution was concentrated to obtain the crystals of 3,3'-dicarboxy-2,2'-bipyridyl. The crystals may be recrystallized from alcohol-water as solvent. The yield is 85 per cent of theoretical.

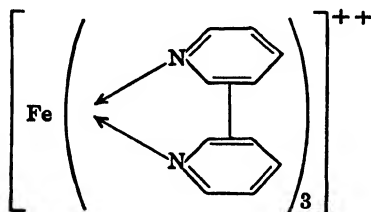
**Oxidation of 1,10-phenanthroline ferrous perchlorate.** The oxidation procedure previously described was applied without change to this compound. The yield was approximately the same per cent.

**Decarboxylation of 3,3'-dicarboxy-2,2'-dipyridyl.** Four grams of the dicarboxylic acid was mixed with 20 grams of biphenyl. This mixture was placed in a reaction flask and heated to 250-275° C., using a Woods' metal bath. After maintaining this temperature for 15 minutes the reaction was assumed complete. The mixture was treated with a large excess of dilute hydrochloric acid before it had cooled enough to solidify and finally filtered from the biphenyl which separated upon cooling. The last small amount of biphenyl was removed by steam distillation. The flask contents were then made alkaline with sodium hydroxide and again steam distilled until the distillate gave no further color with ferrous ions.

After acidifying the distillate with dilute hydrochloric acid it was concentrated to a small volume. The concentrate was made alkaline with sodium hy-

dioxide and the bipyridyl extracted with ether. Evaporation of the solvent yielded 1.2 g. of the bipyridyl or a 47 per cent yield.

**Detection of iron.** Ferrous salts in solutions of mineral acids react with 2,2'-dipyridyl to form a soluble, deep red complex having the following structure:



Ferric salts do not react under the same conditions, and this makes possible the detection of very small quantities of ferrous iron in the presence of large quantities of ferric salts. Ferric iron may be detected after a preliminary reduction with a suitable reducing agent.

Other ammine-forming metallic ions in acid solution also react with 2,2'-dipyridyl, but give only weak colorations, and when a sufficient quantity of the reagent is used they do not interfere with the test for iron. Large quantities of halides and sulfates reduce the solubility of the ferrous-dipyridyl compound in water, so that in the presence of these ions a red precipitate is formed; this does not, however, interfere with the iron test.<sup>2,4,5</sup>

Cuprous salts yield highly colored dipyridyl cuprous complexes, and these interfere with the detection of the red color which is characteristic of ferrous ions.<sup>6,37</sup>

**Procedure.** Place a drop of the solution to be tested in the depression of a spot plate and add a drop of a 2 per cent solution of 2,2'-dipyridyl in dilute hydrochloric acid or alcohol. A red or pink color appears depending upon the amount of iron present.

This reaction may be carried out as a spot test by applying drops of the solution to be tested to a strip of filter paper (Schleicher & Schull No. 589) which has been impregnated with an alcoholic solution of the reagent and dried.

Large quantities of ferrous salts can be detected by the procedure described above, even though ferric salts are present, since the red color of the ferrous complex is easily visible in the presence of the yellow color of ferric salts. If only traces of ferrous salts are present, however, the slight pink coloration may be masked by the yellow color of a concentrated ferric salt solution. This may be eliminated by converting the ferric ion into colorless  $[\text{FeF}_6]^{-3}$  by the addition of a little potassium fluoride.

**Procedure.** Place a drop of the acidified solution to be tested in a porcelain microcrucible, which has been lined with paraffin, and decolorize the yellow solution by adding a few crystals of potassium fluoride. Then add a drop of a 2 per cent alcoholic or dilute hydrochloric acid solution of 2,2'-dipyridyl. A red or pink color appears if ferrous salts are present.



The thiocyanate test for iron is not satisfactory in the presence of large amounts of mercury salts, since the thiocyanate ion is converted into slightly ionized mercuric thiocyanate or into the double thiocyanate of mercury. The prussian blue reaction is also uncertain due to the formation of yellow mercury ferrocyanide. The following test for iron in mercury salts is recommended by Feigl and Hamburg:<sup>4</sup>

**Procedure.** Heat 1-2 drops of the solution to be tested with a little 2 per cent alcoholic solution of 2,2'-dipyridyl, and add a little sodium sulfite and sodium chloride. A pink color appears immediately if only traces of iron are present.

The sodium chloride is added to form the compound  $\text{Na}_2\text{HgCl}_4$ , which prevents the formation of the white insoluble double salt of mercuric chloride and 2,2'-dipyridyl.

Hamburg and Feigl<sup>4</sup> have also used 2,2'-dipyridyl to detect iron in alumina and pyrolusite:

**Procedure.** Grind a small quantity of alumina to a fine powder and fuse with potassium bisulfate in a porcelain crucible. Dissolve the melt in water and add sodium sulfite, and 1-2 drops of a strongly acidified solution of 2,2'-dipyridyl. A pink color appears if iron is present.

To detect iron in pyrolusite, powder the material and dissolve by warming with a little hydrochloric acid and a little 3 per cent hydrogen peroxide. Add sodium sulfite and a little solid 2,2'-dipyridyl to the solution. A more or less intense pink color forms depending upon the amount of iron present.

Hackl<sup>7</sup> has used 2,2'-dipyridyl in a microtest for ferrous oxide in silicates, and regards this as one of the most reliable tests. Szebelledy and Ajtai<sup>8-10</sup> have proposed the following test for the detection of as little as 0.001% of ferrous iron:

**Procedure.** Place a few drops of the solution to be tested in a 5 ml. porcelain microcrucible and add 0.1 ml. of a 0.01 per cent solution of *p*-phenetidine hydrochloride, 1 drop of a 2 per cent alcoholic solution of 2,2'-dipyridyl and 0.1 ml. of a 0.2 per cent solution of hydrogen peroxide measured exactly by means of a micropipet. In the presence of as little as 0.001% of ferrous iron, a red color appears immediately. With ferric iron, the color appears only after heating for 1-5 minutes on a water bath. A blank test prepared similarly remains colorless, or only faintly pink.

In a recent critical review of the reagents used for the detection of ferrous iron, Wenger and Duckert<sup>47</sup> recommend 2,2'-dipyridyl as one of the most satisfactory.

**Determination of iron.** Ferrous iron reacts with three moles of 2,2'-dipyridyl to form an intense red complex,  $\text{Fe}[(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{X}_2$ , in which X may be any monovalent acid radical.<sup>2,6</sup> According to Hill<sup>11</sup> the maximum color is obtained between pH 3.5 and 8.5, and the color is not influenced by other cations unless their concentration greatly exceeds that of the ferrous iron. Even in this case interference may be eliminated by the addition of sufficient reagent to insure

the transformation of the iron to the complex cation. Ferric iron has no more effect upon this determination than other ions, except that in higher concentrations the solutions are yellow in color. Buch<sup>41</sup> claims, however, that ferrous iron alone in the presence of ferric iron cannot be determined. By determining the amount of iron present, both before and after reduction, the 2,2'-dipyridyl method is applicable to the determination of both ferrous and ferric iron. Hydrazine hydrate and sodium hyposulfite are suitable for the reduction of ferric iron. Iodides, tungstates and thiocyanic acid interfere with the development of the red color, usually by forming a precipitate. Manganese causes an interfering brown color.<sup>13</sup> Copper does not interfere in concentrations up to 1,000 times that of iron, and pyrophosphate does not interfere.

The colorimetric determination of iron by means of a series of standards method gives results which are accurate to 10 per cent.

**Reagents.** *2,2'-Dipyridyl*: Dissolve 5 g. of 2,2'-dipyridyl in water and dilute to 1 liter.

*Sodium hyposulfite*: Dissolve sodium hyposulfite in water at 40° C. until the solution is nearly saturated, and then add the solution of the reagent until the maximum color (due to iron as an impurity) is developed. Filter on a Buchner funnel and add an equal volume of alcohol to the filtrate to precipitate pure sodium hyposulfite. Allow to stand for 20 minutes and filter. Wash with 70 per cent alcohol until the crystals and the washings are colorless. Then wash with 95 per cent alcohol. Transfer the crystals to a beaker and boil with 95 per cent alcohol for 10 minutes. Filter at once and transfer the crystals to a desiccator which contains concentrated sulfuric acid. The reagent is prepared by forming a 10 per cent solution of the colorless crystals in water.

*Acetate buffer*: Mix 100 ml. of 2 per cent acetic acid solution and 100 ml. of 3 per cent sodium acetate solution.

**Procedure.** To determine iron in grain and plant products,<sup>11,14</sup> wet ash with concentrated sulfuric and nitric acid, expel the excess acid and dilute until the acid concentration is about 0.1 N. Add 25 ml. of acetate buffer solution and 5 ml. of 2,2'-dipyridyl reagent. Then add 5 ml. of sodium hyposulfite reagent and 1 ml. of a saturated solution of sulfur dioxide in water. Dilute to 100 ml. and compare the resulting color with a series of standards similarly prepared. When properly protected these standards can be kept indefinitely.

For determining as little as 0.5 mg. of iron, the colorimetric method described by Hill<sup>11</sup> is excellent, but instead of using the color standards recommended in this process, McFarlane<sup>15</sup> has obtained more satisfactory results by using cobalt nitrate solutions as the standards. Observed through a thickness of 25 mm., a solution of cobalt containing 2.5 mg. of cobalt ion per ml. has a color intensity which is identical to that of a ferrous-dipyridyl solution containing 1.62γ of iron per ml. The following method is described by McFarlane:<sup>15</sup>

**Reagents.** *2,2'-Dipyridyl reagent*: Prepare a 0.004 M solution of 2,2'-dipyridyl by dissolving 63.2 mg. of the reagent and 1 ml. of N hydrochloric acid in water and diluting to 100 ml.

**Buffer solution:** A buffer solution of pH 4.7 is prepared by mixing equal parts of 0.2 N acetic acid, prepared from redistilled glacial acetic acid, and 0.2 N iron-free sodium hydroxide.

**Cobalt nitrate solution:** Dissolve 1.235 g. of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 100 ml. of distilled water. One ml. of this solution contains 2.5 mg. of cobalt.

**Procedure.** Transfer an aliquot of the solution to be analyzed, which does not exceed 5 ml., to a 10 ml. glass stoppered measuring cylinder. Add 1 ml. of the reagent solution and 0.25 ml. of 0.004 N titanous chloride solution or a small quantity of solid sodium hyposulfite. Dilute to 10 ml. with the acetate buffer solution, mix and compare in a colorimeter with the test solution set at 25 mm., and the cobalt nitrate solution adjusted to match. The iron content in  $\gamma$  per ml. is obtained from the following equation:

$$\frac{\text{Reading of standard}}{25} \times 1.62 = \gamma \text{ Fe per ml.}$$

The most satisfactory results using this method are obtained with iron concentrations ranging from 0.25 to 3.0 $\gamma$  of iron per ml. Thiel and van Hengel<sup>16</sup> have reported that iron can be determined satisfactorily with 2,2'-dipyridyl by applying the principle of absolute colorimetry.

Ferrous iron may be determined in the presence of aluminum, magnesium, zinc, mercury, copper, phosphoric acid and organic substances by the following procedure:<sup>18</sup>

**Procedure.** Acidify slightly an aliquot of the sample which contains 50-100 $\gamma$  of ferrous iron, and add 1 ml. of 10 per cent sulfuric acid, 1 ml. of 20 per cent phosphoric acid, 0.4 ml. of a 1 per cent alcoholic solution of 2,2'-dipyridyl and 10 ml. of 20 per cent ammonium acetate solution. Then dilute to exactly 100 ml. and allow to stand in the dark for 30 minutes. Determine the extinction coefficient photometrically and compare with a blank.

To determine ferric iron in the presence of the above substances, use the following procedure:<sup>18</sup>

**Procedure.** Acidify slightly 20 ml. of a solution containing 50-100 $\gamma$  of ferric iron and add 10 per cent sulfuric acid until the sulfuric acid content of the solution is about 0.5-1.0 per cent. Then add 2.0-2.5 ml. of a saturated sulfurous acid solution, boil for 2 minutes and cool. If the odor of sulfur dioxide is not detected in the solution, add an additional 0.5 ml. of saturated sulfurous acid solution. Then add 0.4 ml. of a 1 per cent 2,2'-dipyridyl solution and 10 ml. of 20 per cent ammonium acetate. Allow to stand for 1 hour, and dilute to exactly 100 ml. and determine the extinction coefficient as directed above. In the presence of phosphoric acid the solution should stand for 24 hours instead of 1 hour.

Moss and Mellon<sup>25</sup> recently carried out a study of the colorimetric determination of iron by means of 2,2'-dipyridyl, and report that the maximum absorption of the iron complex of 2,2'-dipyridyl occurs at 522  $m\mu$ . The molecular extinction coefficient in this wave length is 8650. Beer's law is valid for this

reagent in the region of maximum absorption. The pH may vary between 3.0 and 9.0. Titanous chloride, sodium hyposulfite and ascorbic acid are recommended for the reduction of ferric iron.

Buch<sup>41</sup> reports that the color of ferrous dipyrldyl obeys Beer's law over the concentration range 0.01 to 0.5 mg. of iron per liter of solution, and that the most suitable pH range is 3-5. He also recommends adding 20 times as much dipyrldyl as there is iron present.

Woods and Mellon<sup>19</sup> have compared the 2,2'-dipyrldyl and the thiocyanate method for the colorimetric determination of iron, and report that the 2,2'-dipyrldyl method is superior to the latter. According to their studies the color is stable for six months and shows a close conformity to Beer's law. The color may be developed over a pH range of 3.5-8.5, and there is no effect upon the color by a change of pH within this range. Further, the presence of an excess of reagent is without effect upon the color.

Thiel and co-workers<sup>17</sup> also report that the 2,2'-dipyrldyl method is more satisfactory than the thiocyanate method, but they do not regard sodium hyposulfite as a satisfactory reducing agent. Instead they recommend sulfites and hydroquinone.

Bencze<sup>45</sup> says 1,10-phenanthroline is more satisfactory than 2,2'-dipyrldyl for the iron determination.

Scharrer<sup>14</sup> has applied the 2,2'-dipyrldyl method to the estimation of iron in plant and plant materials and reports that for this purpose it is superior to the thiocyanate method.

Borei<sup>20</sup> has used a spectrophotometric method for the determination of iron in organic matter. This is based upon the formation of the ferrous complex with 2,2'-dipyrldyl and the subsequent determination of the extinction coefficient in a spectrophotometer. Best results are obtained by using monochromatic light of wave length ranging from 4,358 to 5,461 Å. Iron can be measured even in the presence of large amounts of phosphorus, and the error is only 4 per cent of iron ranging up to 0.3γ. With quantities of iron ranging from 3.9 to 500γ the error is reduced to 0.5-1.0 per cent. As little as 0.05γ of iron can be determined by this procedure.

Koenig and Johnson<sup>21</sup> and others<sup>22-25</sup> have used a similar method for the determination of iron in food and biological materials.

Gerber and co-workers<sup>36</sup> have used 2,2'-dipyrldyl for the photometric determination of iron in distilled liquors. Both copper and iron form yellow carbamate complexes which are soluble in isoamyl alcohol, but by converting the iron into unionized ferrous dipyrldyl,<sup>37</sup> which is insoluble in isoamyl alcohol, copper and iron may be separated and determined in the same sample. Iron is best reduced by *p*-hydroxyphenylglycine. Gray and Stone<sup>38</sup> have used 2,2'-dipyrldyl in a direct procedure for iron in beer, making visual comparison with permanent iron standards in a block comparator. Stenger<sup>46</sup> has used 2,2'-dipyrldyl for the determination of iron in magnesium-base alloys. The effect of various ions on the determination of iron with 2,2'-dipyrldyl is shown in Table 10, which is taken from the work of Moss and Mellon:<sup>25</sup>

TABLE 10.—EFFECT OF VARIOUS IONS UPON THE IRON DETERMINATION WITH 2,2'-DIPYRIDYL

Ion	Added As	Present P.p.m.	Error Per Cent	Amount Permissible P.p.m.
Ag <sup>+</sup>	AgNO <sub>3</sub>	25	11	5
Be <sup>++</sup>	Be(NO <sub>3</sub> ) <sub>2</sub>	50	0	50
Cd <sup>++</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub>	50	0	50
Co <sup>++</sup>	Co(NO <sub>3</sub> ) <sub>2</sub>	50	5	20
Cr <sup>+++</sup>	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	50	7.5	15
Cu <sup>++</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub>	5	0	5
Hg <sup>+</sup>	HgNO <sub>3</sub>	10	5.5	5
Hg <sup>++</sup>	Hg(NO <sub>3</sub> ) <sub>2</sub>	10	0	10
Mn <sup>++</sup>	MnSO <sub>4</sub>	75	2	75
Ni <sup>++</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub>	20	5	10
Th <sup>++++</sup>	Th(NO <sub>3</sub> ) <sub>4</sub>	100	0	100
Ti <sup>++++</sup>	Ti(SO <sub>4</sub> ) <sub>2</sub>	37	5	20
Zn <sup>++</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	10	7	5
Zr <sup>++++</sup>	Zr(NO <sub>3</sub> ) <sub>4</sub>	50	0	50
B <sub>4</sub> O <sub>7</sub> <sup>-</sup>	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	100	2	100
CHO <sub>2</sub> <sup>-</sup>	HCO <sub>2</sub> H	100	0	100
C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> Na	100	0	100
C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	5	50	0
CN <sup>-</sup>	KCN	10	0	10
Cr <sub>2</sub> O <sub>7</sub> <sup>-</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	100	0	100
(Cr)				
MoO <sub>4</sub> <sup>-</sup>	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	10	3	7
NO <sub>2</sub> <sup>-</sup>	KNO <sub>2</sub>	50	2	50
VO <sub>3</sub> <sup>-</sup>	KVO <sub>3</sub>	50	2	50
WO <sub>4</sub> <sup>-</sup>	Na <sub>2</sub> WO <sub>4</sub>	10	3	7

When a colored aqueous solution of the ferrous complex of 2,2'-dipyridyl is filtered, some of the color is usually adsorbed by the filter paper. The quantity of the material adsorbed depends upon the area of the paper, and the concentration of the iron, but it always varies somewhat with different types of paper. With some filter paper the adsorption decreases slightly with increasing pH, but, as a rule acid-treated filter papers have a minimum adsorption at pH5. Because of the error introduced by this adsorption, it is advisable to carry out colorimetric iron determinations in dilute solutions, and to filter the solutions if necessary through sintered glass or quartz, which do not adsorb the colored complex. If paper must be used, the results are improved by first saturating the paper with some of the solution before filtering the aliquot which is to be tested.<sup>26</sup>

**Separation of iron.** The complex cation formed with the ferrous iron and 2,2'-dipyridyl is very stable. Iron is not precipitated from solutions of this complex by means of ammonia, nor does it react with potassium ferricyanide to form Turnbull's blue. Thus, if ferric iron is reduced to the ferrous state, and the resulting solution is treated with 2,2'-dipyridyl, the ferrous ion is effectively removed from the reaction mixture, and such metals as magnesium,

beryllium, aluminum and titanium may be determined gravimetrically after precipitation with suitable reagents. If a large quantity of iron is present, it may be precipitated as  $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2$  by the addition of ammonium perchlorate.<sup>27</sup>

**Detection of copper.** An intense color reaction is obtained when 2,2'-dipyridyl is added to a solution containing a cupric salt and a reducing agent, such as sodium bisulfite, hydroxylamine or hydrazine. This reaction may be used for the detection of copper,<sup>35</sup> but does not appear suitable for the colorimetric determination.<sup>36</sup>

**Detection of molybdenum.** Molybdenum may be detected by means of a violet color which appears when molybdates are treated with 2,2'-dipyridyl and stannous chloride.<sup>28,29,48</sup>

**Procedure.** Add 2 drops of a 3 per cent alcoholic solution of 2,2'-dipyridyl to the solution to be tested, and add a drop of a solution prepared by dissolving 10 g. of stannous chloride in 20 ml. of concentrated hydrochloric acid. An intense reddish violet color or precipitate forms if molybdenum is present. The method is sensitive to 0.4% of molybdenum in 0.04 ml. of solution.

Rhenium, vanadium and pentavalent arsenic do not interfere with this test, but tungstate interferes by reacting with stannous chloride. This can be avoided by adding tartaric acid, which forms a complex with tungstate.

**Detection of tin.** Tin is detected by means of a reaction between stannic chloride and the ferrous-dipyridyl complex ion.<sup>30</sup>

**Reagent.** Dissolve 0.196 g. of ferrous ammonium sulfate,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and 0.234 g. of 2,2'-dipyridyl in 5 ml. of hot water.

**Procedure.** Place about 0.0005 ml. of the reagent solution on a glass slide, and place near this 0.001 ml. of stannic chloride solution which has been mixed with equal volumes of 0.1 N hydrochloric acid and a saturated sodium chloride solution. Upon mixing these drops, star-shaped crystals and a dark red coloration appear. By means of this reaction as little as 0.001% of stannic tin at a dilution of 1:1,000,000 can be detected.

Zinc and cadmium also react with this reagent.

**Detection of tantalum and columbium.** Tantalum and columbium may be detected by means of dark red crystals which are formed when solutions of tantalum and columbium compounds are treated with the ferrous-dipyridyl reagent described above. This reaction will detect about 0.2% of tantalum and columbium. Large quantities of tungsten and molybdenum interfere.<sup>31</sup>

**Reactions with nickel.** Jaeger and van Dijk<sup>32</sup> have prepared a number of compounds of nickel with 2,2'-dipyridyl. Two of the compounds which have been reported are  $[\text{NiDipy}_3]\text{SO}_4 \cdot 7\text{H}_2\text{O}$  and  $[\text{Ni dipy}(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , in which dipy = 2,2'-dipyridyl.

**Salts of the ferrous dipyridyl complex.** The ferrous dipyridyl complex cation,  $[\text{Fe dipy}_3]^{++}$ , forms with many anions salts which are useful analytically. Poluektov and Nazarenko<sup>33</sup> have described the microchemical detection of various anions through the formation of characteristic crystalline precipitates containing these complexes. The ferrous dipyridyl reagent which they used is prepared as follows:

**Reagent.** Dissolve 0.196 g. of ferrous ammonium sulfate,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and 0.234 g. of 2,2'-dipyridyl in 5 ml. of hot water.

Many anions form insoluble compounds with this reagent. The sensitivities of these precipitation reactions are given in Table 11.

TABLE 11.—REACTIONS OF FERROUS DIPYRIDYL REAGENT WITH THE ANIONS

Ion	Sensitivity	Remarks
Chloride	1:10	Reacts in neutral and acid solutions to form only a slight dust-like precipitate. Reacts in neutral and acid solutions to form only a slight dust-like precipitate. Reacts in neutral or weakly ammoniacal solution.
Bromide	1:50	
Iodide	1:1,000	
Thiocyanate	1:5,000	
Molybdate	.....	
Tungstate	.....	
Vanadate	1:40,000	
Dichromate	1:6,000	
Permanganate	1:12,500	
Perrhenate	1:2,000–1:1,000	
Ferrocyanide	1:5,000	
Ferricyanide	1:30,000	
Nitroprusside	1:20,000	
Chloroplatinate	1:100,000	

Feigl and Miranda<sup>40,44</sup> have further studied the precipitation of anions with the ferrous dipyridyl complex, and report that insoluble compounds are formed with molybdic, tungstic, phosphomolybdic, phosphotungstic and periodic acids, and also with the following complex anions:  $\text{HgI}_4^{-2}$ ,  $\text{BiI}_4^{-}$ ,  $\text{CdI}_4^{-2}$ ,  $\text{Ni}(\text{CN})_4^{-2}$ ,  $\text{Co}(\text{CN})_6^{-3}$ ,  $\text{Zn}(\text{CN})_4^{-2}$ ,  $\text{Cd}(\text{CN})_4^{-2}$ , and  $\text{Hg}(\text{CNS})_4^{-2}$ .

All of these precipitates are crystalline, and range in color from red to blackish-red, which indicates that the ferrous dipyridyl complex constitutes the chromophoric constituent of the various salts.

The formation of these insoluble salts may be used for the detection and determination of various substances. For example, Feigl and Miranda<sup>40,44</sup> report that mercury, bismuth, nickel, zinc, cadmium and phosphate may be determined quantitatively by procedures based upon this principle. In general, however, these methods offer little advantage over other methods which are in use.

**Detection of cadmium.** The precipitation of red  $[\text{Fe dipy}_3]\text{CdI}_4$  may be made the basis for a very sensitive spot test for cadmium. If the test is carried out in an ammoniacal solution, it is successful even in the presence of both copper and zinc. The simplicity of the procedure and the sensitivity of the reaction make it superior to all other spot tests used for cadmium. In carrying out the test it is important to adhere to the conditions given in the following procedure:

**Reagent.** Dissolve 0.25 g. of 2,2'-dipyridyl and 0.146 g. of ferrous sulfate heptahydrate in 50 ml. of water. Add 10 g. of potassium iodide and shake vigorously for 30 minutes. Filter, and use the clear filtrate as the reagent. This reagent is stable, but may become cloudy on standing. This solution is still useful after filtering.

**Procedure.** Place a strip of thick filter paper (S. and S. 601 or Whatman <sup>120</sup> across the top of a small beaker or crucible. Place a drop of the neutral, slightly acid, or ammoniacal solution to be tested on the paper. Before the spot is adsorbed, treat with a drop of the reagent. If cadmium is present, the red precipitate is left as a spot or ring. A blank test is necessary only if small quantities of cadmium are present. As little as 0.05% of cadmium at a dilution of 1:1,000,000 may be detected by this method.

Metal ions which form insoluble or complex iodides interfere with this test. By treating the solution with ammonium hydroxide, however, interfering lead, mercuric, bismuth, stannous, and stannic ions are precipitated as the hydrous oxides, and may be removed by filtration. The test may be applied to the ammoniacal filtrate. Copper and zinc, which also interfere, are not precipitated with ammonium hydroxide, but are converted to the complex  $\text{Cu}(\text{NH}_3)_4^{++}$  and  $\text{Zn}(\text{NH}_3)_4^{++}$  ions, which are without effect on the test. The only interfering ions remaining in the filtrate are  $\text{Ag}(\text{NH}_3)_2^+$  and thallium. These are removed by acidifying with hydrochloric acid, and filtering off the precipitated chlorides of thallium and silver. The filtrate is then made ammoniacal, filtered if necessary, and the filtrate tested for cadmium.

The cadmium complex,  $[\text{Cd dipy}_2](\text{SCN})_2$  is formed by adding an alcoholic solution of 2,2'-dipyridyl and an aqueous solution of ammonium thiocyanate to a solution of cadmium sulfate. From the optical properties of these crystals, it is possible to detect small quantities of cadmium.<sup>42,43</sup> Zinc forms a similar complex, but both zinc and cadmium can be identified either alone or together.

**Detection of zinc.** Zinc is detected by the formation of the complex zinc dipyridyl thiocyanate as described in the preceding section.

**Determination of cadmium.** Cadmium is quantitatively precipitated from a solution containing potassium iodide by the addition of the ferrous pyridyl complex. Although the precipitate corresponds to the formula  $[\text{Fe dipy}_3]\text{CdI}_4$ , it cannot be weighed directly for the estimation of cadmium. When washed with water, the precipitate dissolves somewhat, and also decomposes slightly. The method is excellent, however, for the separation of cadmium from copper and zinc, which are not precipitated when precipitation is



carried out in an ammoniacal solution. The following method is recommended by Feigl and Miranda:<sup>44</sup>

**Procedure.** Precipitate cadmium as described in the section on the detection of cadmium, and collect the precipitate on filter paper, or in a filter crucible. Wash well with the diluted reagent, and dissolve in hot 1:4 sulfuric acid. Add an excess of concentrated bromine water, and boil for 10 minutes. Cool the solution, make alkaline with ammonium hydroxide, and then warm. Filter off the precipitate of hydrous iron oxide, and precipitate cadmium in the clear filtrate by adding an ammoniacal solution of mercaptobenzothiazole. Wash with dilute ammonium hydroxide, and dry to constant weight at 110-120° C. The factor for cadmium is 0.2330.

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## 5-NITRO-1,10-PHENANTHROLINE

$C_{12}H_7O_2N_3$

Mol. Wt. 225.18

**Use:** Determination of iron.

5-Nitro-1,10-phenanthroline is a light yellow, crystalline solid melting at 201.5° C.

**Preparation:** Mix 1 g. of 1,10-phenanthroline with 5 ml. of concentrated sulfuric acid and 3 ml. of concentrated nitric acid and keep at a temperature of 120° C. for two hours. Pour the yellow solution onto 50 g. of cracked ice and neutralize the cold solution with 30 per cent sodium hydroxide. Filter, dry and recrystallize from 95 per cent ethyl alcohol.<sup>4</sup>

A similar procedure is carried out as follows: Dissolve 1 g. of 1,10-phenanthroline in 10 ml. of concentrated nitric acid and add this solution to 20 ml. of 95 per cent sulfuric acid. Allow the mixture to stand for 1 hour at 115-20° C. and precipitate the compound by dilution with water and the addition of sodium hydroxide. Purify by recrystallizing from water.<sup>1</sup>

Smith and Richter<sup>4</sup> report that by using fuming sulfuric acid and concentrated nitric acid and allowing the temperature to exceed 120° C., the yield can be materially increased.

**Determination of iron.** 5-Nitro-1,10-phenanthroline, like 1,10-phenanthroline, forms an intense red complex with ferrous ions. This reaction has been used by Mehlig and Hulett<sup>2</sup> for the spectrophotometric determination of iron. 5-Nitro-1,10-phenanthroline seems to have the advantage over 1,10-phenanthroline that the ferrous complex is more stable toward acids than the corresponding complex with 1,10-phenanthroline.

The color may be developed over the pH range of 2.5-9.5. Beer's law is valid over the range 0.1 to 5 p.p.m. of iron.<sup>3</sup>

The following procedure may be used for the determination of iron in ores:

**Reagents.** *5-Nitro-1, 10-phenanthroline reagent:* This is a 0.1 per cent solution of the reagent in 95 per cent ethyl alcohol.

*Hydroxylamine hydrochloride:* Dissolve 10 g. of the compound in sufficient water to make 100 ml. of solution.

*Stannous chloride solution:* Dissolve 56.49 g. of stannous chloride dihydrate in 350 ml. of 6 N hydrochloric acid and dilute to 1 liter with water.

*Standard iron solution:* Dissolve 0.7029 g. of 99.9 per cent ferrous ammonium sulfate hexahydrate in water and dilute to 100 ml. Dilute 10 ml. of this solution to 1 liter with distilled water which has been made slightly acid with hydrochloric acid. Each ml. of this diluted solution contains 0.01 mg. of iron.

**Procedure.** Place 0.5 g. of iron ore in a 250 ml. beaker and add 25 ml. of concentrated hydrochloric acid. Cover with a watch glass and warm the mixture on a hot plate until all of the solid has dissolved, or until only a white siliceous residue remains. Transfer the solution to a 1 liter volumetric flask, filtering if necessary, and dilute to the mark. Shake thoroughly and measure a 10 ml. aliquot into a 100 ml. volumetric flask. Dilute to the mark and mix well. Transfer a 10 ml. aliquot of this solution to a second 100 ml. volumetric flask, and add 1 ml. of hydroxylamine hydrochloride solution and sufficient water to make the volume about 75 ml. Then add 10 ml. of the 5-nitro-1,10-phenanthroline solution and dilute to the mark. Make transmission measurements of this solution in a 1-cm. cell at 490 and 505 mμ. Repeated readings in a single setting instead of readings at different settings are recommended for routine work. The transmittancy is obtained by multiplying transmission by 100 and dividing by the transmission at the same wave length of a blank solution.

The percentage of iron is calculated from the equation

$$I = I_0 \times 10^{-kcl}$$

in which  $I_0$  represents the intensity of the light of a given wave length entering the system,  $I$  the intensity of the light transmitted by the system,  $l$  the length in centimeters of the solution through which the light passes,  $c$  the concentration

in grams per liter of the substance absorbing the light, and  $k$  the specific extinction coefficient, a constant which is a measure of the absorption due to a single molecule.

The specific extinction coefficient is obtained by determining the transmittances at 490 and 505  $m\mu$  for a series of solutions of known iron content by the method described above.

Results obtained by this method agree within  $\pm 2$  per cent with those given by the bichromate method. Results may be duplicated on the same sample with an accuracy of  $\pm 0.1$ -0.2 per cent. The method is most sensitive for concentrations of iron ranging from 0.5 to 4 p.p.m. The advantages of this method over the salicylic acid spectrophotometric method for iron are its much wider pH range and greater freedom from interference by other ions. Both methods give about equally satisfactory results. The use of 5-nitro-1,10-phenanthroline has the disadvantage of requiring about 2 hours for the full development of the color.

**The use of 5-nitro-1,10-phenanthroline ferrous sulfate complex as a precipitant for various metal cations.** For a complete discussion of the use of 5-nitro-1,10-phenanthroline, see page 93 in the section on 1,10-phenanthroline.

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## 1,10-PHENANTHROLINE

Synonym: *o*-Phenanthroline

$C_{12}H_8N_2$

Mol. Wt. 180.20

Beil. Ref. XXIII, 227.

**Use:** Detection of cerium, chromium and tellurium.

Determination of cerium, copper and iron.

1,10-Phenanthroline is a white crystalline powder which melts at 93-94° C. It usually is obtained as the monohydrate, but becomes anhydrous at 117° C. It is soluble in about 300 parts of water and 70 parts of benzene, and is soluble in alcohol and acetone.

**Preparation:** Mix 125 g. of glycerol, 125 g. of 100 per cent sulfuric acid and 50 g. of arsenic pentoxide in a 1 liter flask, which is fitted with a thermometer, stirrer and reflux condenser. Heat to 115° C. and add, all at once, 25 g. of *o*-phenylenediamine. Heat carefully to 140° C. and keep at that temperature for 2 hours. Carefully avoid increasing the temperature above 140° C. Pour the reaction mixture into water, make strongly alkaline, and allow to stand for 24 hours. Separate the tarry product, wash and dry at 110° C. until hard and

brittle. Grind the mass to a powder and extract with benzene in a Soxhlet extractor until the residue no longer gives a red color with ferrous sulfate. About 10-20 hours is necessary for the extraction. The crude product which crystallizes on evaporation of the benzene is purified as follows: Dissolve in dilute acid, add alkali until a small tarry precipitate forms, discard this precipitate and finally precipitate the base with an excess of alkali. Recrystallize from water as the monohydrate. Use decolorizing charcoal during the crystallization.<sup>1,2</sup>

The following method is taken with slight modification directly from the work of Smith and Richter:<sup>21</sup>

**8-Nitroquinoline:** Mix 138.1 g. of 2-nitroaniline, 368.2 g. of dry glycerol (prepared by passing a current of air dried with calcium chloride through the glycerol for three hours at a temperature of 170-180° C.), and 172.4 g. of arsenic pentoxide in a dry three-necked flask. Equip the flask with a glycerol-sealed stirrer in the center, a thermometer dipping into the liquid in one side arm, and a pyrex condenser fitted with a calcium chloride drying tube in the remaining arm. With the stirrer in rapid motion, add 220 g. of sulfuric acid in a thin stream through the condenser at such a rate as to maintain the temperature below 130 degrees. When the addition of acid is complete (15-20 min.), replace the drying tube and keep the temperature at 130-135° C. for one hour. Usually, the heat of reaction will suffice for about the first half hour and then apply heat carefully with an electric cone heater or an oil bath, but never directly with a burner. After an hour at 130-135° C. there is usually little danger of the reaction getting out of control; then increase the applied heat and allow the mixture to reflux actively for six more hours. If the heat is applied indirectly, the stirrer may be stopped after the second hour as there is danger of the material "caking" due to localized heating. During the refluxing stage the reaction mixture reaches a maximum temperature and gradually drops as the reaction proceeds for several hours.

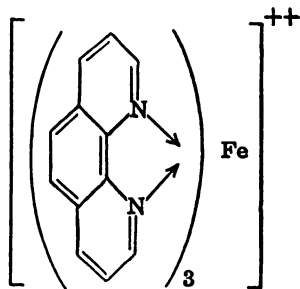
After cooling to room temperature, pour the reaction mass into 3 liters of water, add 30 g. of decolorizing carbon and warm the mixture and stir for one hour. Neutralize the cold filtrate slowly with 1:1 aqueous ammonia, and filter the crude product, which is suitable for the next step. A small portion recrystallized from methanol melts at 91-92° C.

**8-Aminoquinoline:** Mix the crude 8-nitroquinoline obtained above with 500 ml. of dilute (1:4) hydrochloric acid and stir during the gradual addition of 175 g. of iron dust. Warm the mixture on the steam bath and stir for one hour. Cool and make alkaline with 10 per cent aqueous sodium hydroxide, and extract the crude 8-aminoquinoline with hot benzene. Remove the benzene by distillation and purify the product by distillation in vacuo and/or recrystallization from ligroin. Yield 70-75 g. (m.p. 70-72° C.).

**1,10-phenanthroline:** Apply the general procedure to a mixture of 36.0 g. (0.25 mole) of 8-aminoquinoline, 92.1 g. (1.0 mole) of glycerol, 43.7 g. (0.19 mole) of arsenic pentoxide and 50.0 g. of sulfuric acid. Pour the reaction mass into 750 ml. of water, neutralize in the cold with 1:1 ammonia and extract the

black syrupy residue with boiling benzene. After removal of the benzene, purify the product by distillation in vacuo and/or recrystallization. The monohydrate, m.p. 99-100° C., crystallizes from an ethanol-water mixture or moist benzene. The anhydrous compound, m.p. 117° C., is obtained by recrystallizing from a benzene-petroleum ether mixture, after distilling off the water of hydration. Yield of monohydrate 25-27 g.

**Determination of iron.** 1,10-Phenanthroline forms intensely colored and stable coordination complexes with ferrous iron, cobalt, nickel, copper, cadmium and zinc. Blau<sup>8</sup> first observed the deep red complex of ferrous iron with 1,10-phenanthroline, and assigned to it the following formula:



The intensity of the color produced is determined by the amount of iron present when there is an excess of 1,10-phenanthroline. The formation of this color has been applied satisfactorily to the determination of small quantities of iron in various materials.<sup>4-10,22</sup> The color intensity is independent of acidity in the pH range 2-9, but below pH 2 the color develops slowly and is much weaker. There is close conformity of the colored solution to Beer's law. The complex is stable, and solutions show no change in color after many months.<sup>5</sup>

Hydroxylamine and hydroquinone are the most satisfactory reducing agents for converting ferric iron to the ferrous state. Hydroquinone is said to be a more satisfactory reducing agent than hydroxylamine in the presence of citrates.<sup>9</sup>

Fortune and Mellon<sup>6</sup> claim that the 1,10-phenanthroline method is one of the most satisfactory for determining 0.1-6.0 p.p.m. of iron in 1-ml. comparison tubes.

Woods and Mellon<sup>12</sup> have reported that the 1,10-phenanthroline method for determining iron is superior to the well known thiocyanate method, and for general work is superior to methods using ferron, mercaptoacetic acid, salicylic acid and salicylaldehyde. The method using thiocyanate is not easily adaptable for use with a photoelectric colorimeter, since ferric thiocyanate is somewhat unstable in acidic aqueous solutions. Bencze<sup>28</sup> reports that 1,10-phenanthroline is superior to dipyriddy, salicylic acid and sulfosalicylic acid for the iron determination.

One great advantage in the use of 1,10-phenanthroline lies in the possibility of using it in slightly acid solutions, so that hydroxides, phosphates and other salts of many metals are not precipitated.

Saywell and Cunningham<sup>6</sup> recently reported that iron can be determined

quantitatively in small concentrations in fruit juices and other products by comparing the color of the ferrous phenanthroline complex with that of a series of standards. Hummel and Willard<sup>7</sup> applied the method to the determination of iron in biological materials.

**Reagent.** Dissolve 0.5 g. of 1,10-phenanthroline monohydrate in 100 ml. of distilled water and warm until the solution is complete.

**Hydroquinone solution:** Dissolve 1 g. of hydroquinone in 100 ml. of sodium acetate-acetic acid buffer solution of pH 4.5. Store in a refrigerator and discard as soon as any color develops.

**Procedure.** Heat the material to be analyzed overnight in an electric muffle at 450-500°C. Dissolve the ash in the smallest possible quantity of 1:3 hydrochloric acid and filter into a 100 ml. volumetric flask. If the first ashing is incomplete, wash the paper and ash thoroughly with distilled water and re-ash as before. Dissolve the ash as previously described and filter into the same volumetric flask. Dilute to volume and use an aliquot portion which contains a quantity of iron suitable for the final color measurement. If the color is to be measured in a photometer, the aliquot should contain 0.01-0.7 mg. of iron, or if in a visual colorimeter, the aliquot should contain 0.2-0.5 mg. of iron.

Measure similar aliquots of the unknown solution into a 25-ml. volumetric flask and a test tube, and add 2 M sodium acetate to the test tube until the color corresponds to a pH of 3.5, using 5 drops of LaMotte bromophenol blue. Now add to the aliquot in the flask the same volume of 2 M sodium acetate which was required to give a pH of 3.5 with the aliquot in the test tube, and follow with 1 ml. of 1 per cent hydroquinone solution and 1 ml. of 1,10-phenanthroline solution. Mix thoroughly, allow to stand for 1 hour, and then dilute to volume. The final measurement is carried out with a colorimeter or a photometer.

If a colorimeter is used, prepare a series of standards by dissolving electrolytic iron in sulfuric acid and diluting properly with distilled water. The standards should contain 0.2-0.5 mg. of iron. Standards and unknown should be prepared simultaneously. The results are not accurate if the quantity of iron in the unknown differs from that of the standard by more than 25 per cent.

The addition of sodium acetate to solutions of ash of various materials frequently yields turbid solutions which cannot be read directly in a photometer. Cowling and Bene,<sup>9</sup> working with plant ash, overcame this difficulty by adding ammonium citrate before adjusting the pH to 3.5 with sodium acetate. Bandemer and Schaible<sup>25</sup> have found that sodium citrate can be used to advantage to replace sodium acetate for adjusting the acidity in the determination of iron in eggs and poultry ration.

If the pH is adjusted before the addition of 1,10-phenanthroline, the rate of color development is influenced by such factors as time interval between addition of the reagents, temperature of the solutions, type and quantity of phosphate present, amount of citrate used, and the length of time solutions

stand before being read in a photometer. If sodium citrate is added before the hydroquinone and 1,10-phenanthroline, and at a temperature above 20° C., these factors cause no serious error. Under these conditions, the maximum color appears after 30 minutes.

The following method has been described by Bandemer and Schaible.<sup>25</sup>

**Reagents.** *1,10-Phenanthroline solution:* Add 150 ml. of almost boiling distilled water to 0.5 g. of 1,10-phenanthroline contained in a 200-ml. volumetric flask. Allow to cool and dilute to volume. Store in a refrigerator, and discard if any color develops.

*Hydroquinone solution:* Dissolve 1 g. of hydroquinone in 100 ml. of distilled water. Store in a refrigerator, and discard if any color develops.

*Sodium citrate solution:* Dissolve 250 g. of sodium citrate in distilled water and dilute to 1 liter.

*Standard iron solution:* Dissolve 1 g. of electrolytic iron in 50 ml. of 10 per cent sulfuric acid and dilute to 1 liter with distilled water. This solution contains 1 mg. of iron per ml. of solution.

**Procedure.** Transfer to a 25-ml. volumetric flask an aliquot of the unknown solution containing a quantity of iron which is suitable for the range of the photometer. Add 1 ml. of the hydroquinone solution, 2 ml. of the 1,10-phenanthroline solution, and the proper quantity of sodium citrate to bring the pH to 3.5. Dilute to the mark and allow to stand 30 minutes at a temperature above 20° C. Read in a photometer, using as a blank for the 100 setting, a solution prepared in the same manner as the unknown, but containing only the reagents. Use a 1-cm. absorption cell and a 12.5 mm. No. 430 dark-shade blue-green Corning molded glass filter. Convert the readings into concentrations of iron by referring to a curve prepared from the iron standard in exactly the same manner.

Mehlig and Hulett<sup>18</sup> have used 1,10-phenanthroline for the spectrophotometric determination of iron in iron ore. This method depends upon the reduction of ferric iron with hydroxylamine and measurement of the light transmittancy at 490  $m\mu$  and 500  $m\mu$  of the colored solution produced by the action of ferrous iron on 1,10-phenanthroline.

**Procedure.** To approximately 0.5 g. of iron ore, add 25 ml. of concentrated hydrochloric acid and heat until a nearly white siliceous residue remains. Filter, if necessary, into a liter volumetric flask and wash the filter paper thoroughly. Dilute to the mark, mix well and transfer a 10.00 ml. aliquot to a 100 ml. volumetric flask. Dilute to 100 ml., mix and transfer a 10.00 ml. aliquot to a second 100 ml. flask. Add 1.00 ml. of 10 per cent hydroxylamine solution and dilute with water to about 75 ml. Add 10.00 ml. of 0.1 per cent aqueous solution of 1,10-phenanthroline monohydrate and dilute to 100 ml. Mix well and measure the light transmission at 490 and 505  $m\mu$ , using a 1-cm. cell.



The transmittancy is obtained by multiplying the transmission by 100 and dividing by the transmission at the same wave length of a blank solution. The percentage of iron is calculated from the equation

$$I = I_0 \times 10^{-klc}$$

in which  $I_0$  represents the intensity of the light of a given wave length entering the system,  $I$  the intensity of the light transmitted by the system,  $l$  the length in centimeters of the solution through which the light passes,  $c$  the concentration in grams per liter of the substance absorbing the light, and  $k$  the specific extinction coefficient, a constant which is a measure of the absorption due to a single molecule.

The specific extinction coefficients are determined for the color system at 490 and 505  $m\mu$  by determining the transmittancies at those wave lengths of a series of solutions of known iron concentrations as described above.

Fortune and Mellon<sup>5</sup> have studied the effect of various ions upon the colorimetric determination of iron with 1,10-phenanthroline, and report as follows:

- (a) Silver and bismuth yield precipitates.
- (b) Certain divalent metals, such as cadmium, mercury and zinc form slightly soluble complexes with 1,10-phenanthroline, and, moreover, reduce the intensity of the iron color. This interference is reduced by adding a larger excess of the reagent. The maximum permissible concentration of these ions with 2 p.p.m. of iron is 1 p.p.m. of mercury, 10 p.p.m. of zinc and 50 p.p.m. of cadmium.
- (c) Not more than 10 p.p.m. of mercurous mercury should be present at pH 3-9.
- (d) Beryllium in concentrations up to 50 p.p.m. does not interfere if the pH is between 3.0 and 5.5.
- (e) Hexavalent molybdenum does not interfere if the pH exceeds 5.5, but in more acid solutions a turbidity appears.
- (f) Tungstate decreases the intensity of the color, but interference is not serious if the tungsten concentration is less than 5 p.p.m.
- (g) Copper must not be present in concentrations exceeding 10 p.p.m., and in the presence of this element the pH must be adjusted to 2.5-4.0.
- (h) Nickel interferes by changing the hue. Not more than 2 p.p.m. may be present.
- (i) Cobalt yields a yellow color. The concentration should not exceed 10 p.p.m. at pH 3-5.
- (j) Stannous tin should not be present in quantities greater than 20 p.p.m. at pH 2-3, and the concentration of stannic tin should not exceed 50 p.p.m. at pH 2.5.
- (k) Chromic ions change the hue of the solution.
- (l) Sodium and potassium do not interfere in quantities up to 1000 p.p.m.
- (m) Ammonium, arsenite, arsenate, barium, calcium, lead, lithium, magnesium, manganese and strontium do not interfere in quantities up to 500 p.p.m.

(n) Acetate, bromide, chlorate, chloride, citrate, iodide, nitrate, sulfate, sulfite and thiocyanate do not interfere over the applicable pH range in concentrations as high as 500 p.p.m.

(o) Oxalate in concentrations as high as 500 p.p.m. does not interfere if the pH is kept above 6.0.

(p) Tartrate in concentrations as high as 500 p.p.m. does not interfere if the pH is kept above 3.0.

(q) Cyanide interferes seriously. Ten p.p.m. of cyanide ion may be present with 2 p.p.m. of iron with a maximum interference over the applicable pH range of 2 per cent.

(r) Perchlorate may cause a precipitate of 1,10-phenanthroline perchlorate unless present in small quantities.

(s) Nitrite does not interfere if the pH is kept above 2.5.

(t) If pyrophosphate is present, the pH must be above 6.0. At this acidity, 50 p.p.m. of pyrophosphate causes an error of only 1 per cent with 2 p.p.m. of iron. Hummel and Willard<sup>7</sup> found that as much as 50 mg. of pyrophosphate in 25 ml. of solution at pH 3.5 did not interfere in the determination of 0.2 mg. of iron if the mixture was allowed to stand at least 30 minutes after the addition of 1,10-phenanthroline and hydroquinone. Cowling and Benne<sup>9</sup> have stated that interference by pyrophosphate, which is present in the analysis of plant products, is eliminated if the ash is heated for at least 15 minutes with 6 N hydrochloric acid.

(u) Phosphate does not interfere in quantities up to 20 p.p.m.  $P_2O_5$  at pH 2-9.

(v) Fluoride in concentrations up to 500 p.p.m. does not interfere if the pH is kept above 4.0.

(w) Chloride and sulfate do not interfere in moderate quantities.

Asmus<sup>11</sup> has reported that when a colored solution of the ferrous-1,10-phenanthroline ion is filtered, some of the color is usually adsorbed by the filter. The quantity adsorbed depends upon the area of the paper and concentration of iron but varies somewhat with different kinds of paper. With some filter paper the adsorption decreases slightly with increasing pH, but as a rule acid-treated filters have a minimum of adsorption at pH 5. Because of this effect, it is advisable to carry out the colorimetric determination of iron in dilute solutions, and it is best to filter through a sintered glass or quartz filter, which does not adsorb the colored compound. If filter paper must be used, first saturate with some of the solution before filtering the aliquot which is to be tested.

1,10-Phenanthroline has been used for the determination of iron in plant materials,<sup>7,9,14,26</sup> in fruit juices<sup>6</sup> and in spinal fluid.<sup>15</sup>

**Detection of iron.** Iron may be detected by the color reaction with 1,10-phenanthroline. Wenger and Duckert<sup>24</sup> recommend this reagent as one of the most satisfactory for the detection of ferrous iron.

**Determination of copper.** Tartarini<sup>16</sup> observed that 1,10-phenanthroline and copper form a complex which can be reduced with hydroxylamine to give an intensely brown colored cuprous compound. This is formed by treating

an ammoniacal solution of a copper salt with 1,10-phenanthroline and then reducing with hydroxylamine.<sup>22</sup> The order of addition of the reagents is very important: The copper must be in the form of the ammonia complex, and the reagent must be added before the hydroxylamine. The concentration of ammonia is also very important.

The formation of the orange to brown color is due to the complex salt,  $\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{X}$ . Precipitation is prevented by the use of organic solvents which are miscible with water; these also increase the stability of the color. Methyl carbitol appears to be the best of the organic reagents used, and the color formed in its presence is stable for 24 hours. The following procedure is used for the determination of copper:<sup>17,22</sup>

**Procedure.** The solution to be analyzed should contain 0.01-0.5 mg. of copper. If it is necessary to remove metals which are precipitated with ammonia, make the solution just alkaline to litmus with concentrated ammonium hydroxide, filter into an Erlenmeyer flask, and wash the precipitate with 3 N ammonium hydroxide until the washings run through colorless. Remove the flask and transfer the washed precipitate to the original container, and dissolve with a minimum quantity of concentrated sulfuric acid. Precipitate as before with ammonium hydroxide and collect the filtrate in the same Erlenmeyer flask. Evaporate the solution to 15 ml. and neutralize to litmus with 6 N hydrochloric acid or ammonium hydroxide as needed. Then add in the following order: 2 ml. of 6 N ammonium hydroxide, 10 ml. of 0.1 per cent 1,10-phenanthroline solution, 1 ml. of 10 per cent hydroxylamine hydrochloride and 20 ml. of methyl carbitol. Dilute to 50 ml. with water, mix well and measure or compare the color by any of the usual methods.

Only cadmium, cobalt, nickel and zinc, of those metals whose compounds are insoluble under the conditions of the determination, interfere seriously. Cyanide, dichromate and thiosulfate interfere somewhat. Large quantities of metavanadate may interfere. For solutions containing 5 p.p.m. of copper, the following ions may be present in concentrations of 500 p.p.m. without causing an error greater than 2 per cent: ammonium, calcium, lithium, magnesium, potassium, sodium, acetate, arsenate, arsenite, bromide, chlorate, chloride, fluoride, iodate, iodide, molybdate, nitrate, nitrite, phosphate, perchlorate, periodate, silicate, sulfate, sulfite, tetraborate and tungstate.

The following ions precipitate: aluminum, antimony, bismuth, cerium, chromium, cobalt, iron, lead, manganese, mercury, titanium, thorium, uranium, zirconium and also beryllium if present in concentrations exceeding 100 p.p.m.

**Detection and determination of cerium.** Charlot<sup>18</sup> has used 1,10-phenanthroline for the determination of cerium. This method depends upon the oxidation of cerous to ceric cerium with sodium bismuthate, and the subsequent titration of the ceric salt with a solution containing 0.025 mole of  $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]^{++}$ . A 0.025 M solution of 1,10-phenanthroline-ferrous sulfate is prepared by dissolving the stoichiometric quantity of 1,10-phenanthroline monohydrate in a 0.025 M solution of ferrous sulfate in water.

Cerium may be detected qualitatively by heating the sulfuric acid solution with ammonium sulfate and sodium bismuthate until a brisk evolution of gas occurs, and then filtering and adding 1 drop of a reagent containing 0.25 g. of 1,10-phenanthroline-ferrous sulfate per liter. In the presence of cerium a bright blue color is formed, while in the absence of cerium the color is red. This method will detect 2-3 mg. of cerium per liter.

Permanganates, dichromates and vanadates interfere in both the qualitative and quantitative determination. Chloride is rendered harmless by heating with an excess of the bismuthate solution.

**Detection of tellurium and chromium.** Tellurium dioxide does not react with colorless ferric-1,10-phenanthroline complex, but in the presence of chromic acid the reduction of the indicator solution takes place and the red ferrous complex is formed. This reaction can be used for the indirect determination of a fraction of a milligram of chromium. This reaction is based upon the intermediate formation of unstable tetra- or pentavalent chromium.

Tellurium dioxide may be detected by a reversal of this reaction.<sup>19</sup>

**The use of 1,10-phenanthroline ferrous sulfate complex as a precipitant for various metal cations.** The following discussion is taken from the booklet on phenanthroline and substituted phenanthrolines by Smith and Richter:<sup>21</sup>

The phenanthroline and substituted phenanthrolines and their ferrous sulfate complexes may be used as precipitants for a number of metal cations. The cost of these reagents, however, makes a macrochemical operation involving their use as precipitants of somewhat questionable practicability. Such applications would demand a satisfactory procedure for the recovery of the reagents for repeated use. For microchemical operations the methods are entirely feasible. The following procedures illustrate only a few of a large number of possibilities. The methods are subject to many variations. The centrifugal separation of the precipitates involved and the estimation of the cations found by measurement of the volume of the precipitate is but one possible procedure. The determinations might be worked out by weighing the precipitate; by dissolving the precipitate and titrating with a standard oxidant; or by evaluating the solution of the precipitate by determination of the color produced. In the determinations described, the 5-nitro-1,10-phenanthroline ferrous sulfate complex or the free base is used as precipitant. The various substituted phenanthrolines, bipyridyl and terpyridyl all have possibilities. Non-aqueous solvents might be used with considerable advantage. The very high molecular weight of the precipitates involved is conducive to a high degree of precision for both gravimetric and centrifugal volumetric methods of measurement. Colorimetric and oxidimetric estimations of the precipitates are in some ways equally attractive.

**The separation and microdetermination of ferrous iron in the presence of ferric iron, fluorides, sulfates and phosphates.** The procedure depends upon the precipitation of ferrous iron with a slight excess of 1,10-phenanthroline in the presence of fluoride, sulfate, and phosphate, after which an excess of perchloric acid is added. The insoluble ferrous perchlorate complex of 1,10-

phenanthroline is formed, and the amount of ferrous iron present is estimated by measurement of the volume of the precipitate following centrifugation. The fact that fluoride, sulfate, and phosphate do not interfere adds to the value of the procedure, since hydrofluoric, sulfuric and phosphoric acids or mixtures of these acids may be used as solvents for the sample analyzed. An insoluble silicate may therefore be dissolved in a mixture of hydrofluoric and sulfuric acids in an inert atmosphere, and the ferrous iron might possibly be determined by the described procedure applied directly on the solution thus prepared.

**Apparatus.** Standard Goetz tubes used for the determination of phosphorus in steel on a macro-basis following centrifugation, were employed. Their 100-ml. capacity was no disadvantage, although far too large; but the trunnion cups used as their support and the International Equipment Company centrifuge with which they are employed is none the less suitable, and was available. The capillary tubes of the Goetz apparatus for the determination of phosphorus in steel was of far too great capacity, and these were replaced by much smaller capillaries. The total capacity of the capillary tube was found to be  $2 \times 10^{-5}$  ml. One millimeter of the capillary tube had a volume of  $8 \times 10^{-7}$  ml., and its total length was approximately 25 ml. The remainder of the equipment is standard laboratory apparatus, including a suitable weight buret to increase precision.

**Reagents.** *1,10-Phenanthroline solution:* Dissolve 1.485 g. of 1,10-phenanthroline monohydrate in sufficient water to make 100 g. of solution (0.025 M).

*Ferrous sulfate solution:* Dissolve 0.5 g. of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in sufficient water to make 100 g. of solution. A little sulfuric acid is added to prevent hydrolysis. This solution contains 1 mg. of iron per g. of solution.

*Ferric sulfate solution:* Dissolve 1.5 g. of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  in sufficient water to make 100 g. of solution. This solution contains 3 mg. of iron per g. of solution.

*Sodium fluoride solution:* Dissolve 1 g. of sodium fluoride in sufficient water to make 100 g. of solution.

*Potassium sulfate solution:* Dissolve 0.2 g. of potassium sulfate in sufficient water to make 100 g. of solution.

*Sodium phosphate solution:* Dissolve 2.0 g. of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in sufficient water to make 100 g. of solution.

*Perchloric acid:* This is a 1 molar solution.

**Illustrative Procedure.** From a weight buret, 0.3 g. of 1,10-phenanthroline solution (0.006 millimoles for precipitating iron, and excess) was added to the Goetz tube in which the capillary was previously filled with water. To this was added 0.3 g. of ferric sulfate solution (equivalent to 0.9 mg. of iron) and 0.1 g. of ferrous sulfate solution (equivalent to 0.1 mg. of iron or 0.002 millimoles). To the resulting red complex was added 0-15 ml. of 1 N perchloric acid (approximately 100 times excess for the reaction). After centrifuging for 4 minutes

TABLE 12.—THE DETERMINATION OF FERROUS IRON USING 1,10-PHENANTHROLINE AND PERCHLORIC ACIDS AS PRECIPITANT

No.	Material Determined	Weight Taken	Material Added	Ratio of Ions	Volume ppt. ml. $\times 10^{-3}$	Weight Anion Found	Weight of Precipitant	Number of Samples
1	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.25	.....	....	3.10	....	0.20	4
2	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	.....	....	5.50	....	0.30	4
3	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.75	.....	....	8.00	....	0.40	4
4	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	1.00	.....	....	11.20	....	0.50	4
5	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	1.25	.....	....	14.40	....	0.60	4
6	$\text{Fe}^{++}$		$\text{Fe}_2(\text{SO}_4)_3$					
7	$\text{Fe}^{++}$	0.10	0.3	1-2	5.6	0.101	0.30	4
8	$\text{Fe}^{++}$	0.10	0.6	1-6	5.6	0.101	0.30	4
9	$\text{Fe}^{++}$	0.10	0.9	1-9	5.6	0.101	0.30	4
10	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.05	0.9	1-18	3.2	0.06	0.30	4
11	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$		$\text{NaF}$					
12	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.75	3.0	1-4	8.8	0.77	0.40	2
13	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	5.0	1-10	5.7	0.52	0.30	3
14	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	10.0	1-20	5.6	0.51	0.30	3
15	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	20.0	1-30	5.7	0.52	0.30	3
16	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$		$\text{K}_2\text{SO}_4$					
17	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	5.0	1-10	5.6	0.51	0.30	2
18	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	10.0	1-20	5.6	0.51	0.30	2
19	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	15.0	1-30	5.6	0.51	0.30	2
20	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	20.0	1-40	6.4	0.57	0.30	2
21	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$		$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$					
18	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	5.0	1-10	5.6	0.51	0.30	2
19	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	10.0	1-20	5.6	0.51	0.30	2
20	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	15.0	1-30	5.6	0.51	0.30	2
21	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.50	20.0	1-40	5.6	0.51	0.30	2

TABLE 13.—MINIMUM PRECIPITANT REQUIREMENTS AND CALIBRATION DATA FOR THE DETERMINATION OF  $\text{ClO}_4^-$ ,  $\text{IO}_4^-$ ,  $\text{S}_2\text{O}_8^{2-}$ , AND  $\text{MoO}_4^{2-}$  ANIONS

No.	Sample	Sample Weight mg.	Precipitant ml. 0.025 M. Solution	Volume ppt. ml. $\times 10^{-4}$	Samples
1.....	$\text{KClO}_4$	0.50	0.25	0.00	2
2.....	$\text{KClO}_4$	0.50	0.35	3.20	5
3.....	$\text{KClO}_4$	0.50	0.50	11.30	7
4.....	$\text{KClO}_4$	0.50	0.75	14.40	7
5.....	$\text{KClO}_4$	0.50	0.85	14.40	5
6.....	$\text{KClO}_4$	0.50	1.00	15.20	5
7.....	$\text{NaIO}_4$	1.00	0.20	2.40	3
8.....	$\text{NaIO}_4$	1.00	0.30	6.40	3
9.....	$\text{NaIO}_4$	1.00	0.35	8.40	3
10.....	$\text{NaIO}_4$	1.00	0.50	9.60	3
11.....	$\text{NaIO}_4$	1.00	0.75	11.40	3
12.....	$\text{NaIO}_4$	1.00	1.00	12.20	3
13.....	$\text{K}_2\text{S}_2\text{O}_8$	0.50	0.25	0.00	3
14.....	$\text{K}_2\text{S}_2\text{O}_8$	0.50	0.35	6.80	3
15.....	$\text{K}_2\text{S}_2\text{O}_8$	0.50	0.50	10.40	3
16.....	$\text{K}_2\text{S}_2\text{O}_8$	0.50	0.75	13.00	3
17.....	$\text{K}_2\text{S}_2\text{O}_8$	0.50	1.00	13.60	3
18.....	$\text{Na}_2\text{MoO}_4$	0.50	0.10	5.60	3
19.....	$\text{Na}_2\text{MoO}_4$	0.50	0.20	15.64	3
20.....	$\text{Na}_2\text{MoO}_4$	0.50	0.30	18.40	3
21.....	$\text{Na}_2\text{MoO}_4$	0.50	0.40	17.60	3
22.....	$\text{Na}_2\text{MoO}_4$	0.50	0.50	18.40	3
23.....	$\text{Na}_2\text{MoO}_4$	0.50	0.60	19.20	3

at 2,000 r.p.m. the height of the precipitate was 7 mm. which is equivalent to  $5.6 \times 10^{-6}$  mg., corresponding to 0.101 mg. of iron.

This procedure was applied to ferrous sulfate alone, varying the size of the sample, and then in the presence of ferric sulfate up to 20 times excess compared to ferrous iron; sodium fluoride up to 30-fold excess; potassium sulfate 30-fold excess; and sodium dihydrogen phosphate up to a 40-fold excess. The results of these separations are given in Table 12.

The first 5 values of Table 12 were used to make the calibration graph shown in Fig. 1. The values in the remainder of Table 12 are obtained from this graph.

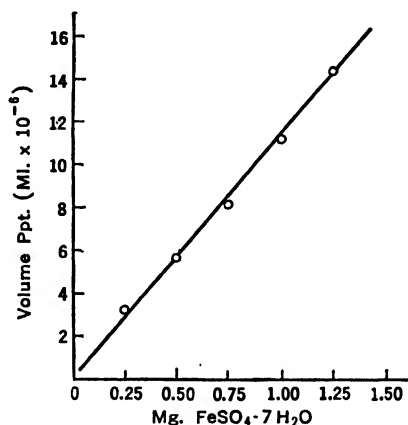


FIG. 1. Calibration curve for Fe determination.

TABLE 14.—THE DETERMINATION OF PERCHLORATE, PERSULFATE AND PERIODATE IN THE PRESENCE OF CHLORATE, SULFATE AND IODATE: 5-NITRO-1,10-PHENANTHROLINE FERROUS SULFATE AS PRECIPITANT

Deter- mination of	Weight Sample mg.	Substance Added	Weight Substance Added mg.	Ratio of Ions	Volume Ppt. $\text{ml.} \times 10^{-6}$	Weight Found mg.	No. Samples
$\text{KClO}_4$	0.375	$\text{KClO}_4$	3.0	1:8	10.3	0.370	5
	0.375	$\text{KClO}_4$	6.0	1:16	10.4	0.370	3
	0.375	$\text{KClO}_4$	7.5	1:20	10.4	0.370	3
	0.375	$\text{KClO}_4$	15.0	1:40	10.4	0.370	3
$\text{K}_2\text{S}_2\text{O}_8$	0.40	$\text{K}_2\text{SO}_4$	2.0	1:5	9.60	0.40	4
	0.20	$\text{K}_2\text{SO}_4$	2.0	1:10	1.60	0.20	4
	0.20	$\text{K}_2\text{SO}_4$	4.0	1:20	1.60	0.20	4
	0.50	$\text{KIO}_3$	2.5	1:5	4.00	0.51	4
$\text{NaIO}_4$	0.50	$\text{KIO}_3$	5.0	1:10	4.20	0.51	4
	0.50	$\text{KIO}_3$	10.0	1:20	4.00	0.50	5



Data for similar calibration graphs and for the determination of minimum precipitant requirements in the case of the precipitation of perchlorates, periodate, persulfate, and molybdate are given in Table 13. In all cases 5-nitro-1,10-phenanthroline was used as precipitant.

The data of Table 13 were used to determine the minimum amount of precipitant required for complete precipitation of the various anions, such as  $\text{ClO}_4^-$ ,  $\text{IO}_4^-$ ,  $\text{S}_2\text{O}_8^{2-}$ , and  $\text{MoO}_4^{2-}$ .

The determination of perchlorate, periodate, and persulfate in the presence respectively of chlorate (reduced to chloride in the presence of perchlorate, with  $\text{SO}_2$ ), iodate, and sulfate, has been studied. The results are shown in Table 14. The separation of molybdate from tungsten is not satisfactory.

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## 1,10-PHENANTHROLINE DERIVATIVES

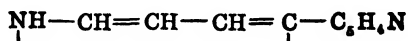
A number of derivatives of 1,10-phenanthroline have been prepared and studied as analytical reagents. Among these are the 5-chloro-, 5-bromo-, 5-methyl-, nitro-, and 5-nitro-6-methyl-derivatives. In general these reagents react like 1,10-phenanthroline, and can be used for the colorimetric determination of iron.<sup>1,2</sup>

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## 2-(2'-PYRIDYL) PYRROLE



Mol. Wt. 144.15



**Use:** Detection of aluminum, cadmium, cobalt, copper, iron, nickel and zinc.

**Preparation:** Shake vigorously 18 g. of potassium pyrrole with a solution of 12 g. of  $\alpha$ -chloropyridine in 20 ml. of benzene and warm for 24 hours at 160° C. Pour off the benzene solution and extract the residue with boiling benzene. Combine the benzene extracts and evaporate the benzene. Fractionally distill the residual oil at 16 m.m. pressure. Pure N-( $\alpha$ -pyridyl) pyrrole distills between 140-145° C. This compound is transformed into 2-(2'-pyridyl)pyrrole by superheating the vapor.<sup>1</sup>

**Reactions with metals.** A solution prepared by dissolving 1 g. of 2-(2'-pyridyl) pyrrole in 10 ml. of alcohol forms complexes with copper, zinc, iron, cobalt, nickel, cadmium and aluminum. These compounds have structures similar to that of the ferrous salt (page 66). The copper salt yields a green precipitate from an ammoniacal solution.<sup>1,2,3</sup>

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## 2-[2'-PYRIDYL]QUINOLINE



Mol. Wt. 206.22



**Use:** Detection of gold and platinum.

2-[2'-Pyridyl] quinoline is a crystalline solid melting at 99° C. It is insoluble in water, but is soluble in most organic compounds.

**Preparation:** Mix 4.84 g. of *o*-aminobenzaldehyde in 30 ml. of alcohol with 4.84 g. of 2-pyridylmethylketone in 10 ml. of alcohol. Add 3 ml. of N potassium hydroxide solution and heat on a water-bath for 1 hour in a flask equipped with a reflux condenser. Treat the mixture with a little decolorizing charcoal and filter. Add hot water to the filtrate until a turbidity appears and then allow the mixture to stand until the crystals separate.<sup>1</sup>

2-Pyridylmethylketone may be prepared by the dry distillation of a mixture of picolinic acid and calcium acetate.<sup>2</sup> *o*-Aminobenzaldehyde may be prepared according to the method of Bamberger and Demuth.<sup>3</sup>

**Detection of gold and platinum.** 2-[2'-Pyridyl] quinoline forms with chloroplatinic acid an orange-yellow insoluble chloroplatinate. The chloroaurate consists of yellow needles and is practically insoluble in water.<sup>1</sup>

1. A. P. Smirnoff, *Helv. Chim. Acta*, **4**, 802-11 (1921); *C.A.* **16**, 234 (1922).
2. C. Engeler and P. Rosanoff, *Ber.* **24**, 2527 (1891).
3. E. Bamberger and O. Demuth, *Ber.* **34**, 1329 (1901).

## 2,2',2''-TERPYRIDYL

$C_{15}H_{11}N_3$

Mol. Wt. 233.24

**Use:** Detection of cobalt, iron and platinum.

Determination of cobalt and iron.

2,2',2''-Terpyridyl is a white crystalline solid which melts at 88-89° C. It is only sparingly soluble in water but dissolves readily in most organic solvents.

**Preparation:** Terpyridyl is prepared by the dehydrogenation of pyridine in the presence of ferric chloride. The product is obtained along with many other compounds by the fractional distillation of the reaction mixture.<sup>1-3,8</sup> For more details, see page 69.

**Detection and determination of iron.** Morgan and Burstall<sup>1,2</sup> first prepared terpyridyl and observed the color reaction which it yields with ferrous iron. The colored product formed in this reaction is regarded by Morgan and Burstall<sup>1,2</sup> as the complex ferrous-terpyridyl ion, which is similar to that formed with dipyridyl.

Cooper<sup>4</sup> applied this reaction to the detection of iron in sea water. He reports that with this reagent 1.0 mg. of iron can be detected in 1.0 cubic meter of water, or at a dilution of 1:1,000,000,000. According to Cooper,<sup>4</sup> terpyridyl possesses two advantages over dipyridyl, which is the more commonly used reagent: first, terpyridyl appears to be twice as sensitive as dipyridyl and consequently is preferred for low concentrations of iron; secondly, at very high dilution the violet color of the ferrous terpyridyl ion remains violet, whereas the red dipyridyl complex becomes somewhat brownish and may be obscured if the water possesses a brownish tinge.

Moss and Mellon<sup>5</sup> have investigated the use of terpyridyl for the colorimetric

determination of iron with the aid of a spectrophotometer. The terpyridyl complex with ferrous iron resembles the permanganate ion in hue, and its absorption maximum occurs at about 552  $m\mu$ . For solutions containing 0.1 mg. of iron, 1 ml. of a 1 per cent solution in 0.2 N hydrochloric acid develops a maximum color, and the excess of the reagent produces no effect. Variations in the pH of the solution between 3 and 10 do not produce any measurable effect on the intensity or hue of the color. Visual comparison in Nessler tubes is more suitable at concentrations of iron ranging from 0.05 to 2 p.p.m. A solution containing 0.001 p.p.m. of iron develops a slight color with terpyridyl.

Since terpyridyl gives a color reaction only with ferrous iron, it is necessary in determining ferric iron or total iron to reduce the ferric iron to the ferrous condition. Cooper<sup>4</sup> used a 10 per cent solution of sodium sulfite with terpyridyl and allowed 24 hours for the development of the color. Hydroxylamine hydrochloride, which is found to be effective with the phenanthroline method and dipyridyl method, also gives good results with terpyridyl.<sup>7</sup> Hydrazine and sulfurous acid are not recommended.

The following procedure is recommended by Moss and Mellon:<sup>5</sup>

**Reagent.** Terpyridyl is not sufficiently soluble in water to permit the preparation of 0.1 per cent solution. A suitable reagent can be prepared by dissolving the proper quantity of the reagent in a 0.2 N hydrochloric acid solution.

An alternate procedure is to convert the base to the hydrochloride, which is easily prepared by evaporating a small volume of hydrochloric acid containing the desired quantity of the base.

**Procedure.** Dissolve the material containing 1 mg. of iron or less, and transfer the solution to a 100 ml. volumetric flask. Add 2 ml. of 10 per cent hydroxylamine hydrochloride solution and adjust the pH to a point between 3 and 9. Ammonium acetate, 6 N ammonium hydroxide and 6 N hydrochloric acid are suitable for this purpose. Then add 5 ml. of a 0.1 per cent solution of terpyridyl. Dilute to the mark and mix well. Compare the resulting color by any of the usual methods with standards similarly prepared. For photometric measurement, use a filter with a maximum transmission in the vicinity of 550  $m\mu$ .

A number of ions interfere with the determination of iron with terpyridyl, and these must be removed or reduced in concentration to a permissible range before carrying out the determination. Five hundred p.p.m. of the following ions may be present without causing an error greater than 2 per cent: aluminum, ammonium, barium, calcium, cerium, lead, lithium, magnesium, potassium, sodium, strontium, uranyl, acetate, arsenate, arsenite, bromide, carbonate, chlorate, chloride, fluoride, iodide, lactate, nitrate, nitrite, phosphate, oxalate, perchlorate, salicylate, sulfate, sulfite, tetraborate, thiocyanate and thiosulfate.

The effect of various ions upon the determination of iron with terpyridyl is given in Table 15, which is taken from the work of Moss and Mellon.<sup>5</sup> \*

The same iron specific group,  $\text{—N}=\overset{\text{C}}{\overset{\text{C}}{\text{=N}}}\text{—}$ , is present in terpyridyl, dipyridyl and phenanthroline and accordingly these three reagents behave simi-

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larly, and there is little to recommend any one of these in preference to others. Dipyrldyl and phenanthroline are more readily available, although terpyridyl is more sensitive and free from interference due to variations of pH and the presence of various ions. These advantages, however, are scarcely important enough to offset the difficulty in obtaining the reagent.

Terpyridyl forms a colored cobalt complex, while dipyrldyl and phenanthroline give practically no color with cobalt but form highly colored copper and molybdenum compounds. Silver interferes seriously with the dipyrldyl and phenanthroline methods for iron, although as much as 100 p.p.m. does not interfere with the terpyridyl determination. Cobalt and copper cause more interference with terpyridyl than with the other two reagents.

**Detection and determination of cobalt.** Terpyridyl reacts with cobalt salts to form an orange complex ion of terpyridyl and cobalt. The structure of this complex according to Mörjan and Burstall<sup>1,2</sup> is analogous to that of the ferrous complex in which two molecules of the triamine are bound by coordinate bonds to the metallic ion. The formation of this complex has been used by Moss and Mellon<sup>6</sup> for the colorimetric determination of small quantities of cobalt. The method is simple and direct, requiring only the addition of the terpyridyl reagent to a solution containing the cobaltous ion, and the subsequent measurement of the orange color. The color reaction of terpyridyl and cobaltous ions is noteworthy in that an exceptionally wide variation in pH is permissible. No effect on the intensity or hue of the color results from changes in pH between 2 and 10. This range is even greater than that allowable in the determination of iron with terpyridyl. Fading occurs within 24 hours at a pH of 3, thus making necessary the use of freshly prepared standards if the color measurements are to be made visually. Beer's Law is valid for cobalt concentrations between 0.5 and 50 p.p.m.

The following procedure is recommended by Moss and Mellon:<sup>6</sup>

**Reagents.** *Terpyridyl solution:* Prepare a 0.1 per cent aqueous solution of terpyridyl hydrochloride calculated on the basis of the free base. This is accomplished by dissolving a weighed portion of the base in the least possible quantity of 6 N hydrochloric acid, and diluting to the proper volume with iron-free water.

*Standard cobalt solution:* Standard solutions of cobalt nitrate containing 0.5 and 0.05 mg. of cobalt per ml. are prepared by dissolving the proper quantity of the hexahydrate in distilled water and diluting to suitable volumes.

**Procedure.** Dissolve the sample by any suitable method, and, after removing interfering substances, adjust the pH to any value between 2 and 10. Twenty per cent ammonium acetate, 6 N ammonium hydroxide and 6 N hydrochloric acid may be used for this purpose. Dilute this solution in a volumetric flask so that each 100 ml. contains 2-5 mg. of cobalt.

To a 25 ml. aliquot of the above sample, add 5 ml. of 0.1 per cent terpyridyl hydrochloride solution, dilute to 50 ml., and mix well. Compare the resulting color with that of suitable standards by any of the usual methods.

The following ions may be present in concentrations greater than 500 p.p.m. without causing an error greater than 2 per cent in determining 10 p.p.m. of

TABLE 15.—EFFECT OF DIVERSE IONS UPON THE DETERMINATION OF IRON WITH TERPYRIDYL

Ion	Added As	Present p.p.m.	Error Per Cent	Amount Permissible p.p.m.
Ag <sup>+</sup>	AgNO <sub>3</sub>	150	3	100
Bc <sup>++</sup>	Bc(NO <sub>3</sub> ) <sub>2</sub>	50	0	50
Cd <sup>++</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub>	100	0	100
Ce <sup>++++</sup>	Ce(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	500	3	300
Co <sup>++</sup>	Co(NO <sub>3</sub> ) <sub>2</sub>	5	30	0
Cu <sup>++</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub>	5	77	0
Hg <sup>+</sup>	HgNO <sub>3</sub>	10	2	10
Hg <sup>++</sup>	Hg(NO <sub>3</sub> ) <sub>2</sub>	10	0	10
Mn <sup>++</sup>	MnSO <sub>4</sub>	200	0	200
Ni <sup>++</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub>	5	6	0
Th <sup>++++</sup>	Th(NO <sub>3</sub> ) <sub>4</sub>	300	0	300
Zn <sup>++</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	10	0	10
Zr <sup>++++</sup>	Zr(NO <sub>3</sub> ) <sub>4</sub>	50	0	50
AsO <sub>3</sub> <sup>---</sup>	Na <sub>3</sub> AsO <sub>3</sub>	500	2	500
AsO <sub>4</sub> <sup>---</sup>	H <sub>3</sub> AsO <sub>4</sub>	250	1	250
B <sub>4</sub> O <sub>7</sub> <sup>---</sup>	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	500	2.5	400
CO <sub>3</sub> <sup>---</sup>	Na <sub>2</sub> CO <sub>3</sub>	10	5	5
CHO <sub>2</sub> <sup>-</sup>	HCO <sub>2</sub> Na	50	0	50
C <sub>2</sub> O <sub>4</sub> <sup>---</sup>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	5	0	5
C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> <sup>---</sup>	(HO)C(CO <sub>2</sub> H)(CH <sub>2</sub> CO <sub>2</sub> H) <sub>3</sub>	5	18	0
CN <sup>-</sup>	KCN	5	6.5	0
Cr <sub>2</sub> O <sub>7</sub> <sup>---</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	50	0	50
MoO <sub>4</sub> <sup>---</sup>	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	50	0	50
NO <sub>3</sub> <sup>-</sup>	KNO <sub>3</sub>	100	2	100
H <sub>2</sub> PO <sub>4</sub> <sup>---</sup>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	10	46	0
P <sub>2</sub> O <sub>7</sub> <sup>---</sup>	Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	10	44	0
SiO <sub>3</sub> <sup>---</sup>	Na <sub>2</sub> SiO <sub>3</sub>	10	4	5
VO <sub>3</sub> <sup>-</sup>	KVO <sub>3</sub>	75	6	25
WO <sub>4</sub> <sup>---</sup>	Na <sub>2</sub> WO <sub>4</sub>	5	21	0

cobalt: aluminum, ammonium, barium, beryllium, calcium, lead, lithium, magnesium, manganese, potassium, sodium, strontium, thorium, acetate, arsenate, bromide, carbonate, chloride, citrate, fluoride, iodide, nitrate, nitrite, orthophosphate, oxalate, pyrophosphate, silicate, sulfate, sulfite, tetraborate, thiocyanate and thiosulfate.

Iron, cyanide and dichromate must be absent, and antimony, bismuth and tin precipitate under the conditions recommended for the determination. Silver interferes slightly and copper, zinc and cadmium interfere if present in sufficiently high concentrations by causing low results for cobalt. Titanium, zirconium and cerium interfere somewhat, although reduction of the ceric ion with hydroxylamine greatly reduces the interference by cerium. The effect of various ions upon the determination of cobalt with terpyridyl is shown in Table 16, which is taken from the work of Moss and Mellon.<sup>6</sup> The amount permissible, is based upon the determination of 10 p.p.m. of cobalt with an error not to exceed 2 per cent.

TABLE 16.—EFFECT OF DIVERSE IONS UPON THE DETERMINATION OF COBALT WITH TERPYRIDYL \*

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Ion	Added As	Present p.p.m.	Error	Amount Permissible p.p.m.
Ag <sup>+</sup>	AgNO <sub>3</sub>	100	2	100
Cd <sup>++</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub>	500	4	250
Ce <sup>+++</sup>	Ce(NH <sub>4</sub> ) <sub>4</sub> (SO <sub>4</sub> ) <sub>4</sub>	200	4	100
Cu <sup>++</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub>	5	0	5
Cr <sup>+++</sup>	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	20	3	15
Ni <sup>++</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub>	10	3	5
Ti <sup>+++</sup>	Ti(SO <sub>4</sub> ) <sub>2</sub>	75	3	50
UO <sub>2</sub> <sup>++</sup>	UO <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	100	1	100
Zn <sup>++</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	20	2	20
Zr <sup>+++</sup>	Zr(NO <sub>3</sub> ) <sub>4</sub>	100	2	100
AsO <sub>3</sub> <sup>---</sup>	Na <sub>3</sub> AsO <sub>3</sub>	500	4	300
MoO <sub>4</sub> <sup>---</sup>	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	100	5	50
VO <sub>3</sub> <sup>-</sup>	KVO <sub>3</sub>	20	4	10
WO <sub>4</sub> <sup>---</sup>	Na <sub>2</sub> WO <sub>4</sub>	100	0	100

The most serious objection to the use of terpyridyl is the interference by iron, copper and nickel. When these metals are present, they must be separated before proceeding with the determination.

Nitroso R salt, which is frequently employed for the determination of cobalt, gives more color with from 1-5 p.p.m. of cobalt than does terpyridyl, but for concentrations lower than 0.1 to 0.5 p.p.m. it cannot be used because of the yellow color of the reagent. Nitroso R salt also requires a more careful control of pH than does terpyridyl.

**Detection of platinum.** Potassium chloroplatinate and terpyridyl react slowly at 90° C. in an aqueous solution to form an orange precipitate and an orange-yellow solution.<sup>3</sup>

1. G. T. Morgan and F. H. Burstall, *J. Chem. Soc.* **140**, 1649 (1937).
2. G. T. Morgan and F. H. Burstall, *J. Chem. Soc.* **135**, 20 (1932).
3. G. T. Morgan and F. H. Burstall, *J. Chem. Soc.* **137**, 1498 (1934).
4. L. H. N. Cooper, *Proc. Roy. Soc. (London)*. **B118**, 419 (1935).
5. M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.* **14**, 862-5 (1942).
6. M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.* **15**, 74-5 (1943); *C.A.* **37**, 1669 (1943).
7. W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.* **10**, 60 (1938).
8. G. Frederick Smith and F. P. Richter, *Phenanthroline and Substituted Phenanthroline Indicators*, booklet published by G. Frederick Smith Chemical Co., Columbus, Ohio (1944).

## CHAPTER IV

### PYRAZOLONE DERIVATIVES

#### ANTIPYRINE

Synonym: 1-Phenyl-2,3-dimethylpyrazolone-5

$C_{11}H_{12}ON_2$

Mol. Wt. 188.22

Beil. Ref. XXIV, 27.

**Use:** Detection of antimony, bismuth, cobalt, iron, mercury, nitrite, rhodium, tin, titanium, tungsten and zinc.

Determination of calcium, nitrite, potassium, and titanium.

Antipyrine consists of colorless, odorless, tabular crystals or a white powder. It possesses a slightly bitter taste, and melts at 111-113° C. One gram of the solid dissolves in less than one ml. of water, 1.3 ml. of alcohol, 1.0 ml. of chloroform, and 43 ml. of ether. The aqueous solution is neutral to litmus.

**Preparation:** *1-Phenyl-3-methylpyrazolone:* Add 13.5 g. of ethylacetoacetate to 10 g. of phenylhydrazine and shake vigorously. Remove the oil which is formed, and heat on a water bath for about 2 hours, or until a test portion solidifies when treated with ether. Pour a little ether into the warm liquid, and collect the crystals which separate. Wash with ether and dry at 100° C. Recrystallize from hot water or alcohol. The melting point is 127° C.

*Antipyrine:* Methylate 1-phenyl-3-methylpyrazolone with a methyl alcohol solution of methyl chloride or methyl bromide at 90-100° C., using a slight excess of the methylating reagent. Carry out the methylation in an autoclave fitted with a stirrer. Distill off the alcohol, and dissolve the reaction product in water made slightly alkaline with sodium hydroxide. Extract antipyrine with benzene, and recrystallize, first from benzene, and then from water containing a little animal charcoal.

Antipyrine may also be prepared by heating equal quantities of N,N'-phenylmethylhydrazine and ethylacetoacetate in an oil bath at 130-160° C. The antipyrine is best extracted from the thick oily liquid with boiling water, and the crystals recovered by evaporation of the aqueous solution.<sup>1</sup>

**Detection of antimony, bismuth, and tin.** Caille and Viel<sup>2</sup> have used antipyrine to detect antimony and bismuth in biological fluids. This test for antimony is based on the formation of a golden yellow precipitate when a solution of antipyrine and potassium iodide is added to a solution of antimony trichloride. A brick-red precipitate is formed with solutions of bismuth salts. The Caille-Viel reagent is prepared as follows:

**Caille-Viel reagent.** Dissolve 1 g. of antipyrine and 2 g. of potassium iodide in 30 ml. of water.



The above reactions are very sensitive.<sup>3,4</sup> Antimony is detected at a dilution of 1:20,000; or, if precipitation is carried out on a microscope slide and examined under magnification, a sensitiveness of 1:200,000 is possible.

Since antimony pentiodide gives a brick-red precipitate of antipyrine periodide with the Caille-Viel reagent, the different oxidation states of antimony may be differentiated.<sup>5</sup>

Antimony may also be detected in a mixture of sulfides by means of a spot test procedure.<sup>6</sup>

**Procedure.** Dissolve the precipitate of sulfides obtained in the regular analytical procedure in aqua regia and evaporate to dryness. Add hydrochloric acid and place one drop of the resulting solution on a piece of filter paper. Add 5 drops of 35 per cent formaldehyde, and after 2-3 minutes add one drop of the Caille-Viel reagent. A yellowish-brown stain indicates antimony.

Antipyrine and potassium iodide yield yellow or white precipitates with stannous and stannic chlorides, thereby causing some difficulty in analyzing mixtures of antimony and tin salts. A light yellow color excludes antimony, but an orange shade masks the color of the tin precipitate. Tin may be detected after reduction by the reaction with mercuric chloride. However, if antimony is known to be absent, tin can be detected with the aid of antipyrine.

Copper forms a brown precipitate with the Caille-Viel reagent and must be removed before testing for antimony. This separation may be effected with ammonium polysulfide.<sup>7</sup> Mercury yields a yellow-white precipitate, and iron a rust colored precipitate.

**Detection of cobalt.** Antipyrine is used in a spot test for cobalt.<sup>8,27</sup>

**Procedure.** Dip a strip of filter paper into the solution to be tested and dry on an electric plate. Add a drop of 20-30 per cent antipyrine solution and again dry. A blue green or pale green ring appears after some minutes if cobalt is present. The reaction is sensitive to 0.4 mg. of  $\text{CoCl}_2$  per ml.

Nickel, mercury, alkaline earth metals, and potassium permanganate do not interfere. Iron causes a brown color and copper a lemon-yellow color.

**Detection of titanium.** A drop reaction based on the method of Moser, Neumeyer, and Winter<sup>9</sup> has been proposed for titanium.<sup>10</sup>

**Procedure.** Saturate a piece of filter paper with a 10 per cent tannin solution, and apply one drop of a 20 per cent antipyrine solution. Then place a drop of the solution to be tested on the antipyrine spot. A red-brown coloration forms if titanium is present. One part of titanium in 250,000 parts of solution can be detected.

If iron, chromium, aluminum, cobalt, nickel, manganese, zinc, mercury, lead, copper, cadmium, bismuth, or zirconium is present, moisten the colored spot with 1:4 sulfuric acid. This removes any coloration except the red-brown stain color caused by titanium. Molybdenum causes a brown-green coloration that is not completely eliminated by the sulfuric acid treatment.

**Detection of zinc.** A solution of antipyrine and ammonium thiocyanate yields a precipitate with a solution containing 100 mg. of zinc per liter, but not with a solution containing 10 g. of cadmium per liter; thus zinc may be detected in the presence of one hundred times as much cadmium. Iron and aluminum are the only metals which interfere, and these are easily removed.<sup>11</sup>

**Detection of mercury.** Mercuric ions in slightly ionized mercuric cyanide may be detected with the aid of antipyrine.<sup>8,12,18</sup>

**Procedure.** To 2 ml. of the cyanide solution, add 1 drop of 10 per cent sulfuric acid, a few drops of 5 per cent potassium iodide solution, 1 ml. of 20 per cent antipyrine solution, and several drops of dilute sulfuric acid. A white precipitate of antipyrine iodo-mercurate is formed.

Antipyrine reacts with mercurous nitrate as follows: prepare a solution by dissolving 2 g. of mercury in 20 ml. of nitric acid and add, after several days, 10 drops of 5 per cent sodium nitrite. When 10 drops of this solution are added gradually to 2 ml. of a 1 per cent solution of antipyrine, a white turbidity appears which is converted to a granular white precipitate on shaking. The precipitate disappears on boiling, but on cooling a brick-red color appears.<sup>17</sup>

**Detection of rhenium.** Antipyrine reacts with perrhenates and chlororhenates to form insoluble compounds which may be used for the detection of rhenium.<sup>28</sup>

**Separation of titanium from chromium.** Titanium is precipitated by the addition of 10 per cent tannic acid and 20 per cent antipyrine in N sulfuric acid. This procedure is especially good when only titanium is to be determined. It is most satisfactory when the quantity of titanium ranges from 0.002-0.05 g., although good results are obtained with as much as 0.1 g. of titanium.<sup>9</sup>

**Separation of tungsten.** One of the most satisfactory methods for separating tungsten from bivalent and trivalent metals, and from tin and silicic acid, is to precipitate the tungsten with a mixture of tannin and antipyrine. Precipitation with tannin alone is incomplete, but the addition of antipyrine makes the separation satisfactory.<sup>14,26,29,30</sup>

**Separation of beryllium from tungsten.** Beryllium is best separated from other cations by causing the accompanying ion to form a complex with tannin, but with tungsten precipitation is often incomplete. To remove the last traces of tungsten from the filtrate after the tannin precipitation, add a clear 15 per cent solution of antipyrine and heat on a water bath.<sup>15</sup>

**Determination of phosphoric acid.** Antipyrine may be used to replace the alkaloid in the strychnine-molybdate reaction of phosphates.<sup>16</sup> For details, see section of strychnine.

**Detection of perchloric acid.** Perchloric acid yields a precipitate with antipyrine. This precipitate dissolves when heated, or when treated with an excess of antipyrine.<sup>17</sup>

**Detection of nitrites.** Nitrites react with antipyrine in an acid solution to form a green color, the intensity of which is proportional to the amount of nitrite present. By means of this reaction nitrites may be detected and also determined colorimetrically. Curtman<sup>18</sup> first used the reaction, although it has since been studied and modified by Schuyten,<sup>19-21</sup> Deniges,<sup>22</sup> and Eschaich.<sup>23</sup> According to Deniges,<sup>22</sup> the test is performed as follows:

**Procedure.** To 1 ml. of solution to be tested, add 3-4 drops of sulfuric acid and heat. Cool, and add 0.5 ml. of a 5 per cent aqueous solution of antipyrine. Nitrites produce a greenish-blue to greenish-yellow color. Next add 3 ml. of sulfuric acid. If nitrate is present, the color changes to orange-red, and this color finally changes to carmine-red on dilution with water.

Eschaich has modified the Curtman test as follows:

**Procedure.** To 2 ml. of a 1:10 aqueous solution of antipyrine, add 15 ml. of solution to be tested, and then add 4 drops of a solution prepared by dissolving 5 g. of mercuric oxide in 20 ml. of concentrated sulfuric acid and 80 ml. of water. Stir well, and add a drop of a 5 per cent solution of potassium ferricyanide and again stir. A red color appears with as little as 0.1 mg. of nitrite per liter.

Nitrate may be detected with the aid of this reaction by first reducing to nitrite with amalgamated aluminum wire. Lead peroxide or potassium persulfate may be used in place of the potassium ferricyanide.

**Determination of nitrite.** Nitrite may be determined by the green color which is formed when an acetic acid solution of antipyrine is added to a solution containing nitrite.<sup>20</sup> This reaction is sensitive to 1 part of nitrous acid in 20,000 parts of solution.

**Reagents.** *Antipyrine solution:* Prepare a 10 per cent solution of antipyrine in acetic acid and dilute to 1 per cent when needed.

*Standard nitrite solution:* Dissolve 0.0493 g. of pure sodium nitrite in water and dilute to 1 liter. One ml. of this solution contains 0.01 mg. of nitrite nitrogen.

**Procedure.** Add 5 ml. of 1 per cent antipyrine solution to 5 ml. of the sample solution and compare the resulting green color with a series of standards containing known quantities of nitrite and which have been similarly treated.

This reaction is not influenced by the presence of heavy metals and organic matter, but if ferric salts or free hydrochloric or sulfuric acids are present the green color turns yellow immediately.

**Determination of calcium.** An indirect method for the microdetermination of calcium has been proposed by Mousseron.<sup>24</sup> This method is based on the formation of insoluble  $K_2CaNi(NO_2)_6$ , followed by the determination of the nitrite contained in the precipitate by means of the green color which is formed with antipyrine.

**Reagents.** *Potassium nickel nitrite solution:* Dissolve 10 g. of potassium nitrite in 100 ml. of 30 per cent aqueous nickel nitrate solution. Add 10 ml. of glacial acetic acid and set aside for some time. Filter, and distill the filtrate in vacuo at 60° C. until the volume is about 50 ml. Add 50 ml. of water and repeat the distillation. Do this three times, adding 50 ml. of water each time and distilling to a volume of 50 ml. The purpose of the distillation is to remove acetic acid. Dilute the neutral solution remaining to 100 ml. and add 45 g. of pure potassium nitrite. Allow to stand 24 hours and filter.

*Antipyrine solution:* Dissolve 5 g. of antipyrine in 100 ml. of water.

**Procedure.** Place 5 ml. of a neutral solution containing about 1.0 mg. of calcium in a centrifuge tube, add 5 ml. of the potassium nickel nitrite solution, and let stand 5 hours. Centrifuge, decant the supernatant liquid from the yellow precipitate ( $K_2CaNi(NO_2)_6$ ), and wash, first with two 1-ml. portions of 20 per cent acetone, and then once with a 1:1 ethyl alcohol-ether mixture. Dissolve the precipitate in 7 ml. of water and add 3 ml. of 5 per cent antipyrine and 1 ml. of sulfuric acid. Compare the resulting green solution with standards prepared in a similar manner.

From 0.5 to 1.0 mg. of calcium can be determined in this manner.

**Determination of potassium.** Potassium may be determined indirectly after precipitating as potassium cobaltinitrite, by determining the nitrite content of the precipitate with antipyrine.<sup>24</sup>

**Procedure.** Treat the precipitate of potassium cobaltinitrite, obtained in the usual manner, with 1 ml. of 5 per cent sodium hydroxide, and heat to boiling. Cobalt is precipitated as the hydroxide, while the nitrite remains in solution as sodium nitrite. Separate the precipitate by centrifuging, and wash with 3 successive 1-ml. portions of water. Neutralize the solution and wash water with 1:10 sulfuric acid and dilute to 7 ml. Add 3 ml. of 5 per cent antipyrine solution and 1 drop of concentrated sulfuric acid. Mix and compare with a standard similarly and simultaneously prepared. The standard is prepared by precipitating a solution containing a known quantity of potassium as the cobaltinitrite and treating as described above. This method is accurate to 3 per cent.

The standard potassium solution is prepared by dissolving 1.907 g. of potassium chloride in water and diluting to 1 liter. Each ml. contains 1 mg. of potassium. Other standards may be prepared by suitable dilution.

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## ISOPROPYL ANTIPYRINE

Synonym: 1-Phenyl-2,3-dimethyl-4-isopropylpyrazolone

$C_{14}H_{18}ON_2$

Mol. Wt. 230.28

**Use:** Detection of dichromate, perchlorate and stannous chloride.

Isopropyl antipyrine is a crystalline powder which melts at 101-103° C. It is slightly soluble in water, but is soluble in hydrochloric acid.

**Preparation:** Isopropyl antipyrine is prepared by heating 1-phenyl-3-methyl-4-isopropylpyrazolone with dimethyl sulfate at 125° C. for 3 hours.<sup>1</sup>

**Reactions.** A dilute hydrochloric acid solution of isopropyl antipyrine gives a crystalline precipitate with potassium dichromate, sodium perchlorate and stannous chloride. These reactions are sensitive and characteristic, and have been used by Rosenthaler<sup>2</sup> for the microchemical detection of these substances. The test for stannous chloride is made more sensitive by the addition of potassium iodide. With a mixture of stannous chloride and potassium iodide, isopropyl antipyrine yields dark, orange druses. Bismuth and antimony give no corresponding reaction, but they interfere with the formation of the crystals with stannous chloride.

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**1-PHENYL-3-METHYL-5-PYRAZOLONE** $C_{10}H_{10}ON_2$ 

Mol. Wt. 174.20

Beil. Ref. XXIV, 20.

**Uses:** Detection of cobalt, copper, iron, nickel and silver.

1-Phenyl-3-methyl-5-pyrazolone is obtained as prisms from water. It melts at 127° C. It is almost insoluble in cold water, ether and ligroin, but it is more soluble in hot water, and is quite soluble in alcohol, acids and alkalies.

**Preparation:** Place 10 g. of phenylhydrazine and 12.5 g. acetoacetic ester in a 200 ml. flask and allow the mixture to stand for several hours. Remove the water which separates, and heat the mixture on a water bath for two hours. Cool and stir with a little ether to remove the coloring matter, and then filter and wash with ether. Recrystallize from dilute alcohol or hot water.<sup>1-3</sup>

**Reactions with metals.** The tautomeric form of 1-phenyl-3-methyl-5-pyrazolone is capable of forming metallic salts with the hydroxyl group and complex compounds with the  $-N=N-$  group.

An alcoholic solution of the reagent when added to an alcoholic solution of cupric acetate gives a yellowish-green compound.

An alcoholic solution of cobalt chloride gives a blue crystalline salt; an alcoholic solution of ferric chloride forms a red-brown compound; and an alcoholic solution of nickel chloride gives an amorphous green precipitate.<sup>4,6</sup>

Dubsky and Wintrova<sup>5</sup> have prepared and described the following metallic compounds:

R = anion of 1-phenyl-3-methyl-5-pyrazolone

$CuR_2$	Cocoa-brown: m.p. = 185° C.
$CoR_2$	Ultramarine blue
$Co(OH)R_2$	Dark brown
$AgR$	Forms addition product with second mole of R to form $(C_{10}H_9N_2OAg + C_{10}H_{10}N_2O)$
$AgR_2$	More light-stable than $(C_{10}H_9N_2OAg + C_{10}H_{10}N_2O)$
$AgR_2$	Reacts with pyridine to form addition product, $AgR_2 + Py_2$
$AgR_2$	Reacts with KCl or HCl to form silver chloride and some free chlorine
$FeR_3$	Violet tinged gray: m.p. 198° C.

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**PYRAMIDONE**

Synonym: Aminopyrine, dimethylaminoantipyrene, amidopyrine, dimethylaminophenylidimethylpyrazolone

$C_{13}H_{17}ON_3$

Mol. Wt. 231.29    Beil. Ref. XXV, 452 (672).

**Use:** Detection of antimony, bismuth, bromine, cadmium, chlorine, cobalt, copper, cyanide, gold, iron, iodic acid, lead, nickel, nitric acid, nitrite, osmium, oxides of nitrogen, palladium, platinum, silver and zinc.

Determination of copper, iron and silica.

Pyramidone consists of white or colorless, odorless crystals, or occurs as a white crystalline powder. It melts at 107-109° C. One gram of the solid dissolves in 18 ml. of water, 1.5 ml. of alcohol, 1 ml. of chloroform, 12 ml. of benzene and 13 ml. of ether. The aqueous solution of pyramidone is slightly alkaline, and is readily affected by mild oxidizing agents.

**Preparation:** Dissolve 50 g. of antipyrene in 400-420 ml. of water and 72-73 ml. of 14.3 per cent hydrochloric acid. Cool and add slowly 45.7 g. of 42 per cent sodium nitrite diluted with an equal volume of water. Add 280 ml. of 40-45 per cent sodium bisulfite and heat to boiling. While boiling, pass air through the mixture to remove sulfur dioxide. Concentrate, cool, and treat when cold with 100 ml. of concentrated hydrochloric acid. Allow the mixture to stand 24 hours and filter off the white crystals of sulfoaminopyrazolone. Wash with water and convert to the sodium salt by treating the compound in aqueous suspension in 100 ml. of water with 10 per cent sodium hydroxide until neutral. Add the resulting solution slowly over a period of 3-4 hours to a boiling mixture of 93 ml. of formic acid (0.8 g. per ml.) and 51 ml. of formalin (0.39 g. per ml.), and heat on a water bath for 14 hours. The excess formaldehyde and formic acid can be removed by distillation, or the product may be treated directly with strong alkali with cooling in ice. Filter off the pyramidone crystals, and extract the filtrate with benzene. Take up the separated crystals in the benzene extract, and dry the benzene solution over potassium carbonate. Remove the benzene by evaporation, and then crystallize, first from gasoline, and finally from toluene.<sup>29</sup>

**Detection of copper.** Pyramidone reacts with cupric salts in the presence of ammonium or potassium thiocyanate to form a gray-blue to violet precipitate. This reaction constitutes a very sensitive test for copper.<sup>4,5</sup> According to Kolthoff and Hamer,<sup>5</sup> 1 mg. of copper in 1 liter of solution is detected by this method.

Martini<sup>1-3</sup> recommends the following method for the microdetermination of copper:

**Procedure.** Place 1 drop of a 0.01 per cent solution of the copper salt on a glass plate, and add 1 drop of a cold saturated solution of ammonium thiocyanate and 1 drop of a cold saturated solution of pyramidone. If the solution is not too dilute, a precipitate forms which first appears amorphous, but which soon becomes distinctly crystalline.

The violet color obtained in the reaction of copper with ammonium thiocyanate and pyrimidone is not suitable for colorimetric comparison.<sup>6</sup>

Eschaich<sup>7</sup> has used cyanide and pyrimidone for the detection of small quantities of copper. This test is performed by adding 1 ml. of 10 per cent pyrimidone solution, 1 ml. of a dilute cyanide solution, and 10-12 drops of acetic acid to the solution to be tested. A blue color is obtained in the presence of copper.

**Detection of cobalt.** Cobalt reacts with pyrimidone in the presence of ammonium thiocyanate to give a blue-green color.<sup>1,4,5</sup> This reaction may be used to detect 1  $\gamma$  of cobalt in the presence of 100 times as much nickel. Cadmium, copper, iron and zinc react similarly. Wenger and Duckert,<sup>8</sup> who have studied the various reactions used for the detection of cobalt, claim that the pyrimidone method is less satisfactory than many others which have been employed.

**Detection of zinc.** Zinc may be detected by the white precipitate which is formed when zinc salts react with pyrimidone in the presence of ammonium thiocyanate.<sup>1,4,5,9</sup> As reagents, use a 1 per cent aqueous solution of pyrimidone and a saturated solution of ammonium or potassium thiocyanate. This method is capable of detecting 1  $\gamma$  of zinc at a concentration of 1:10,000. Cadmium, cobalt, copper, iron and nickel interfere.

**Detection of cadmium.** Cadmium, like zinc, yields a white precipitate with pyrimidone and ammonium thiocyanate.<sup>1,5</sup>

**Detection of nickel.** Nickel reacts with pyrimidone and ammonium thiocyanate to give a violet precipitate.<sup>4,5</sup>

**Detection of lead.** Lead yields a precipitate with pyrimidone and ammonium thiocyanate.<sup>5</sup>

**Detection of bismuth.** Pyrimidone, like many other heterocyclic nitrogen bases, reacts with bismuth salts in the presence of potassium iodide to give an orange to yellow precipitate. This reaction may be used for the detection of bismuth.

**Detection of antimony.** Pyrimidone, like many organic nitrogen compounds, reacts with antimony salts in the presence of sodium or potassium iodide to form a yellow precipitate. This reaction may be used for the detection of antimony.

**Detection of iron.** Ferric salts react with pyrimidone and ammonium thiocyanate to give a red to violet color or precipitate.<sup>1,4,13,30</sup> As reagent, use a 1 per cent aqueous solution of pyrimidone and a saturated solution of ammonium thiocyanate. According to Van Urk,<sup>30</sup> this reaction is capable of detecting iron at a dilution of 1:10,000,000. Cadmium, cobalt, copper and zinc interfere.

**Detection of cyanide.** The following reaction may be used for the detection of cyanides:<sup>7</sup>

**Procedure.** Mix 1 ml. of a 10 per cent solution of pyrimidone, 1 ml. of a 0.25 per cent copper sulfate solution and 10-12 drops of glacial acetic acid, and



then add dropwise a solution containing hydrogen cyanide. A blue color soon appears which becomes turbid.

Peset and Aguilar<sup>10</sup> have suggested replacing guaiac with pyramidone in a similar test for cyanide.

**Detection of the platinum metals.** Whitmore and Schneider<sup>11</sup> have studied the use of pyramidone as a microchemical reagent for the detection of the platinum metals. Their results are shown in Table 17.

TABLE 17.—REACTIONS OF PLATINUM METALS WITH PYRAMIDONE

Test Material	Description
RuCl <sub>3</sub>	No apparent reaction.
RhCl <sub>3</sub>	No apparent reaction.
PdCl <sub>2</sub>	A dense, yellow precipitate forms immediately. This consists of a mass of very small, yellow, spindle or boat shaped crystals. Many of these occur in clusters.
Na <sub>2</sub> OsCl <sub>6</sub>	On standing many, bright yellow, irregular crystalline forms develop around the edge of the drop. Among these bright yellow, hexagonal plates of fair size appear. Seeding the drop with the crystals that first form around the edge causes a more abundant development of these hexagonal plates.
IrCl <sub>4</sub>	The test drop is immediately decolorized. No precipitate or crystals are formed.
H <sub>2</sub> PtCl <sub>6</sub>	On standing a short time some irregular, yellow, crystalline structures form around the edge of the drop. Among these there appear some pale yellow, flat, hexagonal plates; also some prisms which appear to be hexagonal in form. Seeding the drop with some of the crystals first formed around the edge causes a more abundant crystal formation.
AuCl <sub>3</sub>	A beautiful bluish purple precipitate forms immediately. This precipitate is made up of very small rounded granules.

**Determination of iron.** Pyramidone reacts with ferric chloride to yield an intense blue-violet color.<sup>12</sup> This reaction may be used in an acid solution for the colorimetric determination of small quantities of iron.<sup>18</sup> In a solution which is 0.1 N in sulfuric acid, the color obtained is dependent upon the acid concentration, but at 0.2 N and greater, the acid concentration has little influence. Excellent results have been obtained with 0.05-3.0 mg. of ferric iron per 100 ml. of solution:

**Procedure.** To 50 ml. of the sample solution, add 5 drops of concentrated sulfuric acid and 10 ml. of a 10 per cent solution of pyramidone in 0.2 N sulfuric acid. Dilute to 100 ml. with 0.2 N sulfuric acid and compare with a standard solution similarly prepared.

**Detection of silver and nitric acid.** When a dilute solution of silver nitrate is added to an aqueous solution of pyramidone, the silver is immediately reduced on warming to yield colloidal silver. The colloidal solution exhibits an intense bluish to reddish-violet color, which may be used for the detection

of silver.<sup>14-17</sup> A large excess of nitric acid does not destroy the color. If only a small quantity of nitric acid is added, the silver dissolves and the color disappears. If nitric acid alone is added, a blue color appears which disappears in the presence of an excess of acid.

**Detection of oxidizing agents.** Various investigators<sup>18-21</sup> have called attention to the color reactions which are obtained with pyrimidone and oxidizing agents. Pevenasse<sup>18,17</sup> first called attention to the blue color which is obtained in the reaction of pyrimidone with nitric acid, and which disappears in the presence of an excess acid. Treating a solution of pyrimidone with mercurous nitrate, silver nitrate or fuming nitric acid yields a blue color, whereas pure nitric acid, lead nitrate, potassium nitrate and sodium nitrate react negatively. All oxidizing agents, except pure nitric acid, when brought into contact with powdered pyrimidone yield a yellow zone which is surrounded by a blue-black ring, and this rapidly changes to a pale blue.<sup>22</sup>

Chlorine gas, bromine vapor, or the oxides of nitrogen can be detected in air by passing the latter through a 10 per cent alcoholic solution of pyrimidone which has been acidified slightly with acetic acid. The test may also be carried out by impregnating filter paper with this solution and allowing to dry in the air to be tested. A violet to violet-red color is obtained if the oxidizing gases mentioned above are present. The test is slightly less sensitive than that obtained by a freshly prepared starch-iodide paper.<sup>23,24</sup> Like other oxidizing agents, iodic acid yields a violet color with pyrimidone. The reaction with iodic acid is quantitative. Each atom of oxygen reacts with 1 mole of pyrimidone.<sup>25</sup>

Pyrimidone reacts with sodium nitrite and sulfuric acid to give a violet color.<sup>12</sup> According to Monferrino,<sup>26</sup> this test is more sensitive if sulfuric acid is replaced by acetic acid.

**Determination of silica.** Silicomolybdic acid is quantitatively precipitated by pyrimidone from an acid solution containing a mixture of silicate and an excess of molybdate. The precipitate is bulky and yellow, and settles rapidly from an acid solution. The compound has been assigned the formula  $(C_{13}H_{17}N_3O)_3 \cdot H_8Si(Mo_2O_7)_6 \cdot 6H_2O$ . The following procedure has been recommended by King and Watson<sup>27</sup> for the determination of silica in animal tissue:

**Procedure.** Dry the tissue at 110° C. and grind to a fine powder in a steel mortar. Transfer a 100 mg. sample to a platinum crucible and add 0.25 g. of sodium carbonate. Fuse the mixture and cool and dissolve in water. Neutralize with 1 N sulfuric acid to methyl orange, which is used externally. Transfer the solution to a 100 ml. volumetric flask and dilute to volume with water. Add 10 ml. each of 1 per cent ferric chloride in 0.02 N hydrochloric acid and 1.5 per cent sodium acetate in 0.028 N sodium hydroxide solution. Pour the mixture into a 500 ml. Erlenmeyer flask, bring rapidly to boiling with agitation and filter. The filtrate contains all the silica and no phosphate or iron.

The basic ferric acetate precipitation may be omitted if phosphate is absent. In this case, dilute the solution to 100 ml. as directed above, and then treat directly with the molybdate reagent as described in the following paragraph.

To the measured filtrate add 5 ml. of 5 per cent ammonium molybdate solu-

tion and 2.5 ml. of 10 N sulfuric acid. Heat for 5 minutes on a water bath, and precipitate with 3 ml. of 0.1 M pyrimidone. This quantity of reagent is sufficient to precipitate 6 mg. of  $\text{SiO}_2$ . Filter through a micro filter funnel containing a piece of Whatman No. 45 filter paper over sintered glass. Wash with ice-cold 0.1 N hydrochloric acid and dry at 60-70° C. for 45 minutes and weigh.

**Detection and determination of phosphorus and molybdenum.** Pyrimidone has been suggested as a reducing agent for the formation of the blue color with the complex phosphomolybdic acids.<sup>28</sup>

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## CHAPTER V

### MISCELLANEOUS HETEROCYCLIC NITROGEN COMPOUNDS

#### ACRIDINE

$C_{13}H_9N$

Mol. Wt. 179.21

Beil. Ref. XX, 459.

**Use:** Detection of bismuth, bromide, cadmium, chloride, cobalt, copper, gold, indium, iridium, iron, mercury, nickel, palladium, platinum, rhenium, thiocyanate and uranium.

Acridine is obtained as colorless crystals. They have a pungent odor and a burning taste. The compound is a skin irritant, and its vapor is a powerful sternutatory. It melts at approximately  $110^{\circ}C.$ , and boils above  $360^{\circ}C.$  (without decomposition). It sublimes at  $100^{\circ}C.$  The compound is slightly soluble in water, but is quite soluble in alcohol, benzene, ether, and carbon disulfide. These solutions exhibit a blue fluorescence.

**Preparation:** *o*-Chlorobenzoic acid: Dissolve 13.7 g. of anthranilic acid in a mixture of 30 ml. of concentrated hydrochloric acid and 75 ml. of water. Diazotize with a solution of 7 g. of sodium nitrite in 25 ml. of water. Before diazotizing, prepare a solution of cuprous chloride by boiling 7 g. of cupric chloride with 50 ml. of concentrated hydrochloric acid diluted with 15 ml. of water and 4-5 g. of copper. Cool the cuprous chloride solution in ice, and to this add slowly and with shaking the solution of the diazo compound. Allow the mixture to stand 4-5 hours at room temperature. Filter off the *o*-chlorobenzoic acid and wash with a little water. Dissolve in hot water containing a little alcohol, add a little decolorizing charcoal and boil. Filter hot, and recover the crystals which separate on cooling. The compound melts at  $137-138^{\circ}C.$ <sup>1</sup>

*Phenylanthranilic acid:* Mix 10 g. of *o*-chlorobenzoic acid, 10 g. of potassium carbonate, 40 ml. of aniline and 0.1 g. of precipitated copper, and boil in a round flask fitted with a short air condenser. Boil at such rate that a little water escapes from the top of the condenser. The reaction is complete in about 3 hours. Remove any unchanged aniline by steam distillation, and filter the residue while still hot. Add a little decolorizing charcoal, boil, and again filter. Precipitate phenylanthranilic acid by adding concentrated hydrochloric acid to the hot filtrate. Allow the mixture to cool and filter. Wash the crystals with a little cold water and dry. Purify by recrystallizing from acetic acid and alcohol. The crystals melt at  $183-184^{\circ}C.$ <sup>2,3</sup>

*Acridone:* Mix 5 g. of phenylanthranilic acid with 35 ml. of concentrated sulfuric acid, and heat together on a water bath for 3 hours. Cool the mixture in ice, and then slowly add 40 ml. of ice water with vigorous shaking and cooling. Filter and warm the precipitate of acridone with 300 ml. of a 2.5 per cent

solution of sodium carbonate to dissolve any unchanged phenylanthranilic acid. Filter, wash the residue with water and dry on a porous plate.<sup>4,5</sup>

**Acridine:** Thoroughly mix the acridone with 12-15 g. of zinc dust, and place the mixture in a thick-walled glass tube which is sealed at one end and bent at a right angle. Cover the mixture with an additional 10 g. of zinc, and clamp the tube to a ring stand so that the closed end of the tube lies horizontally, while the open end extends downward into a beaker. First heat the zinc dust and then the mixture. Acridine is formed by reduction, and sublimes toward the open end of the tube. Dissolve the sublimate in hydrochloric acid, filter if necessary, and precipitate acridine by the addition of sodium hydroxide. Filter, and recrystallize from methyl alcohol to which a little decolorizing charcoal has been added.<sup>6</sup>

**Microchemical reactions.** The heterocyclic nitrogen base, acridine, reacts with the salts of cobalt, zinc, copper, iron, mercury, cadmium, bismuth, uranium, nickel, indium, gold, platinum, palladium, and iridium in the presence of ammonium or potassium thiocyanate to form characteristic precipitates of the acridine thiocyanates. By means of these reactions, the above metals, and also thiocyanates, may be detected. Characteristic crystals are also obtained by the addition of chlorides and bromides to an acridine-copper sulfate mixture, and by the difference in the appearance of the crystals formed with bromides and chlorides, these two ions may be differentiated. Rhenium chloride and the chlororhenic acids may be detected by the formation of characteristic microcrystals with acridine. Solutions of acridine exhibit a blue fluorescence, but this is changed or destroyed by reactions with various cations. A number of qualitative tests have been based on this behavior.

Martini and Langer have studied the complex acridine thiocyanates of a number of metals, and have found several of these easily formed and suitable for the microidentification of the cations which they contain. Originally, Martini<sup>7,16</sup> used acridine for the microdetection of cobalt, iron, zinc, and copper. Microcrystals are prepared in the following manner:

**Procedure.** Place 1 drop of 0.1 per cent metallic chloride solution on an object glass, add 1 drop of 1 per cent ammonium thiocyanate and 1 drop of 1 per cent acridine hydrochloride and stir.

The precipitates formed in these reactions are reported by Martini as corresponding to the following formulas:

$[\text{C}_{13}\text{H}_9\text{N}-\text{HCNS}]_2\text{Co}(\text{CNS})_2$	Blue crystals
$[\text{C}_{13}\text{H}_9\text{N}-\text{HCNS}]_2\text{Zn}(\text{CNS})_2$	Yellow crystals
$[\text{C}_{13}\text{H}_9\text{N}-\text{HCNS}]_2\text{Cu}(\text{CNS})_2$	Brown crystals
$[\text{C}_{13}\text{H}_9\text{N}-\text{HCNS}]_2\text{Fe}(\text{CNS})_2$	Red crystals

The crystals are useful for the identification of cobalt, zinc, copper, and iron.

Langer<sup>8</sup> analyzed the above substances and found the composition of the cobalt and zinc compounds to be the same as that stated by Martini, but he

obtained different results for the iron and copper complexes. According to Langer, the composition of these compounds is represented by the formulas,  $[C_{13}H_9N \cdot HCNS]Fe(CNS)_3$  and  $[C_{13}H_9N \cdot HCNS]CuCNS$ .

More recently, Langer<sup>9</sup> has extended the investigation of the acridine thiocyanate complexes to include a number of other ions. His results are shown in Table 18.

TABLE 18.

Formula	Description	Sensitivity
$Hg(SCN)_4 \cdot H_2(C_{13}H_9N)_2$	Slippery yellow needles	0.5 $\gamma$ Hg
$Bi(SCN)_3 \cdot H_2(C_{13}H_9N)_2 \cdot 6H_2O$	Orange-yellow plates	2.0 $\gamma$ Bi
$Cd(SCN)_4 \cdot H_2(C_{13}H_9N)_2$	Long yellow needles	0.01 mg. Cd
$Cu(SCN)_2 \cdot H(C_{13}H_9N)$	Dark brown powder	5.0 $\gamma$ Cu
$Co(SCN)_4 \cdot H_2(C_{13}H_9N)_2$	Long green crystals	5.0 $\gamma$ Co
$Fe(SCN)_6 \cdot H_2(C_{13}H_9N)_2$	Dark red, almost black prismatic crystals from ferric solutions.	
$UO_2(SCN)_4 \cdot H_2(C_{13}H_9N)_2 \cdot 4H_2O$	Small, light yellow spheres	2.0 $\gamma$ $UO_2^{++}$
$Zn(SCN)_4 \cdot H_2(C_{13}H_9N)_2$	Canary-yellow crystals	0.01 $\gamma$ Zn

The Langer test for copper and iron has been modified by Martini<sup>10</sup> as follows:

**Procedure.** Evaporate a drop of the solution to be tested to dryness on a glass slide. When cool, add 1 drop of pure liquid petrolatum, then 1 drop of a 5 per cent solution of potassium thiocyanate, and finally a drop of a 1 per cent aqueous solution of acridine hydrochloride. As little as 0.1 $\gamma$  of copper or iron may be detected by a microscopic examination of the gray or red crystals.

Using the same procedure, nickel yields blue-green prismatic crystals, and indium light-yellow triclinic crystals. Gold reacts directly with acridine hydrochloride to form elongated yellow crystals, which change to a violet color on the addition of stannous chloride. Platinum, iridium, and palladium give with acridine hydrochloride characteristic precipitates similar to those obtained with gold. The sensitiveness of these four reactions is approximately 0.1 $\gamma$ . Rhodium gives an amorphous precipitate.

Reactions similar to those described above may also be used to detect the thiocyanate ion. Cobalt chloride or cupric chloride with acridine serves as a satisfactory reagent for thiocyanate. With copper, 1.0 $\gamma$ , and with cobalt, 0.1 $\gamma$  of thiocyanate may be detected.<sup>11</sup>

**Microchemical detection of rhenium.** Rhenium chloride dissolves in solutions of hydrochloric acid to form chlororhenic acid,  $HReCl_4$ , which gives a crystalline compound with acridine. These crystals may be used for the microscopic identification of rhenium.  $H_2ReCl_6$  reacts in a similar manner.<sup>12,17</sup>

Wenger and Duckert<sup>18</sup> recommend the acridine reaction as one of the most satisfactory for the microchemical detection of perrhenates. The reagent is capable of detecting 0.16 $\gamma$  of rhenium in 0.01 ml. of solution. Zinc interferes.

**Reactions with chloride and bromide.** Bromides may be differentiated from chlorides by means of an acridine-copper sulfate mixture prepared by adding 4 ml. of a saturated solution of copper sulfate to 1 ml. of 10 per cent solution of acridine in 30 per cent acetic acid. Distinct crystal forms are obtained when crystals of the alkali bromides and chlorides are added to this mixture.<sup>18</sup>

**Fluorescence analysis.** Changes in the intensity of fluorescence of acridine by the addition of solutions of metallic salts may be used to detect various cations.<sup>14</sup> Gotō<sup>15</sup> has used the fluorescence of acridine to detect gold, selenium, tellurium, and chromium. Acridine and potassium iodide precipitate gold, causing the fluorescence to disappear. Selenium and tellurium react similarly. As little as 10γ of chromium as chromate destroys the fluorescence of the reagent in basic solutions.

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## ACRIFLAVINE

Synonym: 2,8-Diamino-10-methochloride acridine, tryptaflavine neutral

$C_{14}H_{14}N_8Cl$

Mol. Wt. 259.71

**Use:** Detection of rhenium.

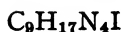
Acriflavine consists of brownish-red, odorless granules or powder. It is soluble in water, but is almost insoluble in chloroform and ether. It is incompletely soluble in alcohol.

**Detection of rhenium.** Acriflavine forms a crystalline perrhenate which may be used for the microchemical detection of the latter.<sup>1,2</sup>

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**ALLYL IODIDE HEXAMINE**

Synonym: Allyliodourotropine, allyl iodide hexamethylenetetramine



Mol. Wt. 308.15



**Use:** Detection and determination of cadmium.

Allyl iodide hexamine is a white crystalline solid. It melts at about 148° C. with decomposition. It is very soluble in water, but is insoluble in ether and chloroform.

**Preparation:** Allyl iodide, prepared according to the method of Datta <sup>1</sup> is added to an equimolecular quantity of hexamethylenetetramine in chloroform.<sup>2</sup>

**Detection and determination of cadmium.** Allyl iodide hexamine reacts with cadmium salts in a neutral or slightly acid solution to form an insoluble crystalline compound corresponding to the formula,  $\text{CdI}_2 \cdot 2(\text{CH}_2)_6\text{N}_4 \cdot \text{C}_3\text{H}_5\text{I}$ . This reaction is used for the detection and determination of cadmium. Cadmium may be detected by a spot method carried out as follows: <sup>3,6,8</sup>

**Procedure.** Place a drop of a very dilute solution of cadmium salt in contact with a drop of a 10 per cent solution of the reagent. Characteristic crystals form at the zone of contact of the 2 drops.

A number of other metals also form precipitates with allyl iodide hexamine, and consequently interfere with the determination of cadmium by this method.

In Table 19 are listed the molar concentrations at which precipitation of various metallic derivatives of the reagent takes place.

TABLE 19.

Salt	Molar Concentration
$\text{SbCl}_3$	$5 \times 10^{-4}$
$\text{Bi}(\text{NO}_3)_3$	$5 \times 10^{-3}$
$\text{FeCl}_3$	$7 \times 10^{-3}$
$\text{PbCl}_2$	$2.4 \times 10^{-7}$
$\text{Hg}(\text{NO}_3)_2$	$4 \times 10^{-4}$
$\text{SnCl}_2$	$6.7 \times 10^{-3}$
$\text{CuCl}_2$	$5 \times 10^{-3}$
$\text{AsCl}_3$	$1 \times 10^{-3}$

Lithium, sodium, potassium, barium, calcium, strontium, magnesium, zinc, aluminum, lanthanum, cerium, zirconium, thorium, stannic tin, manganese, potassium, perrenate, chromium, nickel, and ferrous sulfate do not form insoluble complexes.

Isibasi and Nakazima <sup>4</sup> have studied the relationship of pH to the completeness of precipitation of the cadmium complex of allyl iodide hexamine, and report that the most satisfactory range is from 2.6-5.6.



Isibasi<sup>9</sup> studied the proper drying temperature for the cadmium compound, and recommends a temperature range of 75-105° C.

The precipitate formed with allyl iodide hexamine and cadmium salts is sufficiently insoluble to permit the determination of cadmium.<sup>7</sup> At 25° C., 1.4 mg. of the cadmium complex dissolves in 1.0 ml. of water, and only 0.62 mg. in 1.0 ml. of ethyl alcohol. The precipitate contains 11.44 per cent of cadmium, and may be dried at 105° C. and weighed, or it may be dissolved in ammonia and determined titrimetrically according to the method of Kiba.<sup>5</sup>

**Procedure.** To a solution containing about 1.0 mg. of cadmium per ml., add an excess of a 5 per cent solution of the reagent. Filter and dissolve the precipitate in ammonia. Acidify this solution with hydrochloric acid and titrate potentiometrically with 0.025 N potassium iodate after adding a small quantity of potassium cyanide. The accuracy of this method is said to be about 0.3 per cent.

The reactions involved in the titration are given by the following equations:



Hurd and Evans<sup>2</sup> have conducted a critical study of the method of Evrard<sup>3,16</sup> and report that allyl iodide hexamine is not a trustworthy precipitant for cadmium because of the solubility of the complex and adsorption errors.

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## ANTIPYRINEMETHENAMINE

$\text{C}_{38}\text{H}_{39}\text{O}_8\text{N}_7$

Mol. Wt. 617.67

Beil. Ref. XXIII/XXV(197).



**Use:** Detection of bismuth.

Antipyrinemethenamine is obtained as crystals from alcohol. The free base melts at 259-60° and the hydrochloride at 206°. The compound is insoluble in water, slightly soluble in ethyl acetate, and easily soluble in alcohol, chloroform and acetone.

**Preparation:** Mix a solution of 3.8 g. of antipyrine in 8 ml. of water with 1.06 g. of ammonium chloride in 4 g. 38 per cent formaldehyde. After a few

minutes the entire mass solidifies. Crystallize from alcohol. The compound is obtained as the hydrochloride.<sup>1</sup>

**Detection of bismuth.** Bismuth may be detected by means of the precipitate which forms when an acetic acid solution of a bismuth salt is treated with potassium iodide and a saturated alcoholic solution of the reagent.<sup>2</sup> The precipitate which first forms is voluminous and yellowish-brown in color, but when this is heated on a water bath, it is converted to a heavy, red-brown precipitate of the following composition:



The sensitivity of this reaction is 5γ of bismuth per ml. The limiting concentration is 1:200,000. By means of a spot test, 0.2γ of bismuth may be detected.

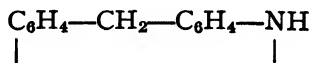
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## DIHYDROACRIDINE

$C_{13}H_{11}N$

Mol. Wt. 181.22

Beil. Ref. XX, 443 (211).



**Use:** Determination of ozone.

Dihydroacridine is obtained as prisms from alcohol. The melting point is 169° C. The compound is easily soluble in hot alcohol and ether, but is insoluble in water. It also dissolves in cold concentrated sulfuric acid.

**Preparation:** Dihydroacridine is prepared from acridine by boiling with sodium amalgam and alcohol or with zinc and hydrochloric acid.

**Determination of ozone.** Small quantities of ozone are determined by the fluorescence produced when the gas is passed through an alcohol solution of dihydroacridine. This reagent is not affected by oxygen at ordinary temperatures, but it is oxidized by ozone to acridine, and the fluorescence of the latter is measured by means of visual photometry. One mole of ozone reacts with 1 mole of dihydroacridine to give one mole of acridine. This method is satisfactory for the determination of quantities of ozone as low as  $10^{-7}$  g. The oxides of nitrogen interfere, since they too convert the reagent to acridine, but hydrogen peroxide is practically without effect.

Dihydroacridine has proved the most satisfactory of the leuco-dyes which have been tried, since its own fluorescence is very small and a correction is easily applied. Alcohol is the best solvent. As reagent, use 3 ml. of 0.0005 per cent solution of the reagent in alcohol.

As little as 2-3 liters of air is sufficient for the test.<sup>2</sup>

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**HEXAMETHYLENETETRAMINE**

Synonym: Urotropin, methenamine, aminoform, hexamine, hexamethyleneamine, ethylmorin, cystamin and cystogen

$C_6H_{12}N_4$

Mol. Wt. 140.19

Beil. Ref. I, 583.

**Usé:** Detection of antimony, bismuth, bromide, cadmium, calcium, cobalt, copper, ferricyanide, indium, iodide, iridium, iron, lithium, magnesium, manganese, mercury, molybdenum, nickel, osmium, palladium, platinum, silver, thorium, tin, vanadium and zinc.

Determination of aluminum, beryllium, bismuth, chromium, cobalt, copper, iron, magnesium, manganese, platinum, tellurium, thorium, titanium, uranium, zinc and zirconium.

Hexamethylenetetramine is a white crystalline solid. It sublimes at about 263° C. without melting and with partial decomposition. It is somewhat volatile at lower temperatures. Upon ignition the compound burns with a smokeless flame. One g. of the solid dissolves in 1.5 ml. of water, 12.5 ml. of alcohol, 10 ml. of chloroform and 320 ml. of ether.

**Preparation:** Hexamethylenetetramine is prepared by passing formaldehyde gas into concentrated ammonium hydroxide, and evaporating the mixture to a syrupy consistency, adding hot absolute ethyl alcohol and allowing to cool. The reagent separates and is filtered, and washed with alcohol and ether.

It is more conveniently prepared by mixing one part of 40 per cent formaldehyde solution with two parts of concentrated ammonium hydroxide and evaporating the mixture to dryness on a water bath.

**Precipitation of metals.** Hexamethylenetetramine reacts as a very weak base, and may be used for the precipitation of certain metallic hydroxides. This property has been used to effect many separations which are necessary in analytical procedures. Compounds of hexamethylenetetramine are known,<sup>1,2</sup> but Lehrmann and Kabat<sup>3</sup> have shown that zinc, ferric iron, chromium and aluminum are precipitated as the hydrous oxides when boiled with aqueous solutions of the reagent.

Lehrmann and co-workers<sup>4</sup> have studied the precipitating action of hexamethylenetetramine upon the cations of the ammonium sulfide group, and have reported their results in Table 20. The results reported in this table were obtained by adding an excess of 10 per cent aqueous solution of the reagent to 20 ml. of a solution containing 100 mg. of the cation.

Ray<sup>6</sup> has studied the reaction of hexamethylenetetramine with various cations and reports that uranium, titanium and zirconium are also precipitated at the boiling temperature by adding a 10 per cent solution of the reagent to a neutral solution of the cations which also contains ammonium chloride.

**Separation of iron from manganese, zinc, nickel and cobalt.** Hexamethylenetetramine reacts as a weak base, and causes the precipitation of ferric

iron as ferric hydroxide from neutral or slightly acid solutions. Manganese is precipitated only in hot neutral solutions. This reaction was suggested by Kollo,<sup>10</sup> and has been used by others,<sup>11,12</sup> for the separation of iron from manganese. The following procedure is taken from the work of Ray and Chattopadhyaya:<sup>12</sup>

TABLE 20.—REACTIONS OF METALLIC IONS WITH HEXA-METHYLENETETRAMINE

Ion	Reagent Precipitation	Reagent + Boiling Precipitation	1 g. $\text{NH}_4\text{NO}_3$ + Reagent Precipitation	1 g. $\text{NH}_4\text{NO}_3$ + Reagent + Boiling Precipitation
Ferric	Complete	Complete	Complete	Complete
Aluminum	None	Complete	Complete	Complete
Chromium	None	Complete	None	Complete
Nickel	None	Partial	None	None
Cobalt	None	Partial	None	None
Manganese	None	Partial	None	None
Zinc	Partial	Complete	None	None
Ferrous	Partial	Partial	Partial	Partial

**Procedure.** To a solution containing 60-150 mg. of iron, add 1 g. of ammonium chloride, unless sufficient acid is present to provide this quantity of the salt on neutralization, and then make the total volume 125-500 ml. Add pure ammonium carbonate solution until the mixture is nearly neutral, and heat to a gentle boil. Slowly add a 10 per cent solution of hexamethylenetetramine until precipitation of ferric hydroxide is complete. Under these conditions all iron is precipitated without contamination by manganese, zinc, cobalt or nickel.

Kundert<sup>62,63</sup> has used hexamethylenetetramine for the precipitation of iron as a preliminary to the determination of nickel and cobalt. Hanus and Vorisek<sup>13</sup> have studied the acetate, succinate and hexamethylenetetramine methods for the separation of nickel and iron. From solutions having a Fe:Ni ratio of less than 40, iron is separated completely by one precipitation by all three methods. When the Fe:Ni ratio exceeds 40, the iron may be separated by a double precipitation, using the acetate or succinate method. With hexamethylenetetramine the precipitate contains nickel after two precipitations. The results obtained with hexamethylenetetramine appear to be inferior to those using the acetate or succinate method.

**Separation of aluminum and iron from calcium, manganese and the alkali metals.** In precipitating aluminum with ammonium hydroxide by the usual methods, carbon dioxide, which is always present in ammonium hydroxide, precipitates some calcium. This causes high results when the aluminum precipitate is ignited to  $\text{Al}_2\text{O}_3$ , and correspondingly low results when calcium is determined after the removal of aluminum. This difficulty can be eliminated by using hexamethylenetetramine, which precipitates aluminum completely without contamination by calcium.<sup>14</sup>

**Procedure.** To the solution containing aluminum and calcium, add 1 g. of solid hexamethylenetetramine, boil for 1 minute, filter while hot, and determine aluminum and calcium by the usual methods.

Charlot<sup>15</sup> has suggested the use of hexamethylenetetramine for the quantitative separation of iron and aluminum from calcium in the presence of phosphates. At a pH of 5.4, iron and aluminum hydroxides and phosphates are completely precipitated while calcium remains in solution, together with any excess of phosphate.

**Procedure.** Neutralize the solution to be analyzed with dilute ammonium hydroxide until a slight precipitate persists. Dissolve this with the aid of a few drops of hydrochloric acid, add 5 g. of ammonium chloride and an equal volume of a solution containing 400 g. of hexamethylenetetramine and 100 ml. of concentrated hydrochloric acid per liter. Allow the precipitate to settle, filter, and wash with 1 per cent ammonium chloride. First wash with a cold solution, and finally with a hot solution. One mg. of aluminum remains dissolved in each 100 ml. of the original solution. Calcium is precipitated from the filtrate at the boiling temperature by the addition of ammonium oxalate. Results are claimed to be within 0.5 per cent of the correct value.

Ostroumov and Bomshtein<sup>16</sup> have described a method for the separation of cations of the third analytical group from calcium, magnesium and the alkali metals by precipitating with hydrogen sulfide in the presence of hexamethylenetetramine.

**Procedure.** To the sample containing not more than 0.5-0.6 g. of the third group elements, calculated as the oxides, add 20-25 g. of ammonium chloride, neutralize with ammonium hydroxide to a slight cloudiness, and clear the solution with a few drops of hydrochloric acid. Dilute the mixture to 150 ml., add a little macerated paper pulp, heat to 60° C., and add dropwise with shaking 6 ml. of pyridine hydrochloride. Pass hydrogen sulfide gas into the mixture. After 10-15 minutes add dropwise with shaking 35 ml. of a 20 per cent solution of hexamethylenetetramine. Place the vessel containing the mixture on a hot plate, and continue to pass hydrogen sulfide into the solution for 45-60 minutes without heating above the boiling point. Remove from the hot plate and continue to treat with hydrogen sulfide until the solution is cool. Filter and wash with a slightly ammoniacal 3 per cent solution of ammonium nitrate. The alkalies, calcium and magnesium may be determined in the filtrate by any of the usual methods.

**Separation of aluminum from manganese, nickel, cobalt and zinc.** Several methods have been suggested for the determination of aluminum by precipitating with hexamethylenetetramine in the presence of manganese, nickel, cobalt and zinc.<sup>6-9</sup> Kozu<sup>8</sup> reports that aluminum alone is precipitated by means of hexamethylenetetramine at room temperature from a solution slightly acidified with sulfuric acid and containing aluminum, manganese, nickel and cobalt.

**Detection and determination of bismuth.** Bismuth may be detected microscopically by means of colorless, refractive, characteristic, insoluble crystals

of hexamethylenetetramine-bismuth chloride,  $3(\text{C}_6\text{H}_{12}\text{N}_4\text{HCl}) \cdot \text{BiCl}_3$ .<sup>17-20</sup> The test is carried out as follows:

**Procedure.** Place on a slide 1 drop of 1:1 hydrochloric acid, and add a drop of 4-5 per cent hexamethylenetetramine solution and then a small quantity of the bismuth compound. A microscopic examination of the crystals reveals the presence of bismuth. By this procedure as little as 0.002 mg. of bismuth can be detected.

Korenman,<sup>21</sup> and Gautier<sup>22,23</sup> have used hexamethylenetetramine with potassium iodide for the detection of lead, tin, bismuth and antimony. This reaction is similar to that obtained with other basic nitrogenous compounds such as antipyrine.

A precipitate of  $\text{BiI}_3 \cdot [(\text{CH}_2)_6\text{N}_4\text{I}]_3$  is formed when a nitric acid solution of bismuth is treated with potassium iodide and hexamethylenetetramine. This precipitate may be weighed as such, or it may be treated with an excess of standard silver nitrate solution in the presence of nitric acid to form silver iodide, which is precipitated. The excess silver nitrite is then determined titrimetrically. Solodovnikov<sup>24</sup> has used both these procedures for the determination of bismuth.

**Determination of copper.** Copper is determined by precipitating with hexamethylenetetramine from a boiling solution.<sup>25</sup> The precipitate is filtered, washed and ignited to constant weight as  $\text{CuO}$ . To determine copper in an ammoniacal solution, add an excess of formaldehyde and then precipitate with hexamethylenetetramine by boiling until all the formaldehyde is expelled. Best results are obtained if the copper is present as the sulfate, since some copper may be lost when the precipitate obtained from the chloride or nitrate is ignited. Precipitation with hexamethylenetetramine permits the separation of copper from the alkali and alkaline earth metals, manganese and magnesium, and also from cadmium, nickel and cobalt after the addition of formaldehyde. It is difficult to separate copper from silver or zinc.

When hexamethylenetetramine and ammonium benzoate are added to a hot, dilute nitric acid solution of a cupric salt, a light blue complex salt of the following composition is obtained:  $\text{Cu}_3(\text{C}_6\text{H}_5\text{CO}_2)_8 \cdot (\text{CH}_2)_6\text{N}_4$ . If washed with water, alcohol and ether, the precipitate may be dried in vacuum and weighed.<sup>26</sup>

**Procedure.** To 50-100 ml. of a solution containing up to 0.1 g. of copper, add a solution of 0.5-1.0 g. of ammonium benzoate and an equal weight of hexamethylenetetramine dissolved in about 20 ml. of water. Stir, filter, and wash with a solution containing 3 g. of ammonium benzoate and 0.3 g. of hexamethylenetetramine per liter. Then wash with water, alcohol and ether, using suction. The precipitate may be dried and weighed as such, or if the quantity is large, it should be ignited to  $\text{CuO}$ . The factor for copper in the complex is 0.1804.

**Detection and determination of manganese.** Ray and Sarkar<sup>27</sup> have used the crystalline compound which is formed when a manganous salt is treated with sodium dithionate and hexamethylenetetramine for the microchemical detection of manganese. A 5 per cent aqueous solution of dithionate and a little solid hexamethylenetetramine are added to a neutral solution of the manganous salt. As little as 0.02% of manganese can be detected in a volume of 0.05 ml. at a dilution of 1:2,500,000 by this method. Nickel, cobalt, and zinc give similar reactions. This method is recommended by Wenger and Duckert<sup>28</sup> as one of the better methods for microdetection of manganese.

Ostroumov<sup>29</sup> has obtained a crystalline precipitate of manganese sulfide by treating solutions of manganous salts with hydrogen sulfide in the presence of hexamethylenetetramine.

**Procedure.** To a slightly acid solution containing not more than 0.5 g. of manganese, add 2 g. of hexamethylenetetramine and heat to 60° C. Saturate with hydrogen sulfide at this temperature. An orange-red, easily filterable precipitate of manganese sulfide is obtained by this treatment. The manganese sulfide can be analyzed by any of the standard methods.

**Detection and determination of cobalt.** The addition of hexamethylenetetramine sulfate and ammonium thiocyanate to a solution of a cobalt salt produces glistening blue triclinic prisms, which may be used for the microchemical detection of cobalt.<sup>30,31</sup> As little as 0.02% of cobalt can be detected by means of the crystals which are formed when a 5 per cent aqueous solution of sodium dithionate and hexamethylenetetramine are added to a neutral solution of a cobalt salt.<sup>27</sup> The hexamethylenetetramine addition compounds with magnesium cobalt cyanide ( $\text{MgCo}(\text{CN})_4$ ) and with iridium magnesium cyanide, ( $\text{MgIr}(\text{CN})_4$ ), are practically insoluble in water, but the addition products with magnesium nickel and magnesium platinum cyanides are soluble. These compounds have been used by Tartarini<sup>32</sup> for the separation of cobalt from nickel, and iridium from platinum.

**Determination of uranium.** Ostroumov and Bomshtein<sup>33</sup> have used hexamethylenetetramine in a procedure for the precipitation of uranium.

**Procedure.** Heat 100 ml. of a nearly neutral solution of uranyl chloride to 60° C., and add 2 g. of hexamethylenetetramine. Introduce hydrogen sulfide for 15 minutes, and then add hydrogen sulfide for an additional 15-20 minutes while heating the mixture on a hot plate. Shake frequently, cool, and allow the precipitate to settle for 15 minutes. Filter, wash with 3 per cent ammonium nitrate containing 2-3 drops of ammonium hydroxide for each 250 ml. of solution, and ignite the residue to  $\text{U}_3\text{O}_8$ .

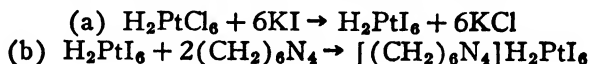
The red precipitate obtained in the above precipitation is believed to be:



It is a crystalline compound and shows negligible adsorption. The above procedure can be used for the separation of uranium from calcium, magnesium and

the alkalis. For a sample containing 0.0490 g. of  $U_3O_8$ , the determination indicated the presence of 0.0491 g.

**Detection and determination of platinum.** Platinum is quantitatively precipitated as  $[(CH_2)_6N_4]H_2PtI_6$  with potassium iodide and hexamethylenetetramine. The reaction is given by the following equation:



When a solution containing platinum and palladium chlorides is treated with hexamethylenetetramine and potassium iodide, the platinum is precipitated.<sup>84</sup> The addition compound of hexamethylenetetramine with iridium magnesium cyanide,  $(MgIr(CN)_4)$ , is practically insoluble while the addition compound with magnesium platinum cyanide,  $(MgPt(CN)_4)$ , is distinctly soluble. The formation of these compounds may be used for the separation of iridium from platinum.<sup>32</sup>

**Detection and determination of thorium.** Vivario and Wagenaar<sup>46</sup> have suggested the use of hexamethylenetetramine for the microchemical detection of thorium, but Wenger and Duckert<sup>36</sup> do not recommend this reaction since it is too general and is not very sensitive. Hexamethylenetetramine has been found useful, however, for the separation of thorium from cerium. The following procedure has been used by Ismail and Harwood<sup>35,57</sup> for the precipitation of thorium in the presence of cerium and other rare earths.

**Procedure.** Warm 100 ml. of the faintly acid solution to be analyzed to 30° C. and add 5 g. of ammonium chloride. Then add dropwise and with stirring, after each addition, a 10 per cent solution of hexamethylenetetramine until a slight excess is present. Allow the precipitate of thorium hydroxide to settle and decant the liquid through a Whatman No. 41 paper. Transfer the precipitate to the paper and wash with a warm 2 per cent ammonium nitrate solution. Dissolve the precipitate on the filter with hot 2 N hydrochloric acid, and wash the paper with hot water. Dilute if necessary, neutralize with ammonia, and make faintly acid to methyl red with hydrochloric acid. Then add sufficient ammonium chloride until it is present to the extent of 5 per cent in the solution, warm, and precipitate as before. Again wash the precipitate and ignite to  $ThO_2$ .

**Detection and determination of magnesium.** When a solution of a magnesium salt is treated with hexamethylenetetramine in the presence of a ferrocyanide, a cream colored crystalline precipitate or a complex magnesium salt is formed. By this reaction 0.002% of magnesium can be detected. A yellow precipitate is obtained with ferricyanide, although this reaction is not quite so sensitive.<sup>27,58,59</sup>

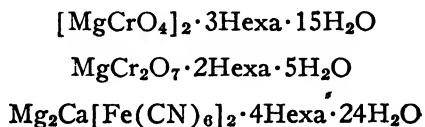
Debucquet and Velluz<sup>37</sup> have determined magnesium by precipitating as  $3CaMgFe(CN)_6 \cdot 4(CH_2)_6N_4 \cdot 40H_2O$ . The precipitate is dissolved in water and the determination is based upon the Prussian blue color which develops on treating with ferric chloride. The determination is carried out as follows:



**Reagent.** Mix a solution prepared by dissolving 8.4 g. of potassium ferrocyanide in 100 ml. of water with a solution containing 4.4 g. of crystalline calcium chloride and 11.2 g. of hexamethylenetetramine in 200 ml. of water. Allow the mixture to stand for 1 hour, filter with suction, and wash with 95 per cent alcohol and ether.

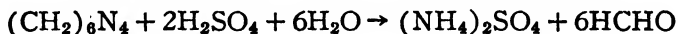
**Procedure.** Evaporate the solution containing about 0.1 mg. of magnesium to dryness, and dissolve in 2 ml. of a solution prepared by treating for 10 minutes 0.5 g. of the reagent with 20 ml. of a 10 per cent solution of hexamethylenetetramine and filtering. Allow to stand for 1 hour, filter through a filter tube and wash 6 times with 1 ml. of 2 per cent hexamethylenetetramine, 3 times with 5 ml. of acetone, and dry with air. Transfer to a tube and add 1 ml. of 10 per cent gum arabic and 1 ml. of 0.03 per cent ferric chloride solution. Stir well and compare the resulting color with that of standards similarly prepared.

A number of other complexes have been proposed containing magnesium and hexamethylenetetramine. Some of these are



"Hexa" represents 1 mole of hexamethylenetetramine.

Blanchetiere and Arnoux<sup>38</sup> have based a semi-micro and microdetermination of magnesium on the quantitative precipitation of magnesium as the complex  $\text{MgI}_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{Hexa}$ , and the determination of iodine by means of silver nitrate. More accurate results are obtained by determining the nitrogen in the precipitate by heating the compound with a definite excess of 0.05 N sulfuric acid and titrating the excess with 0.01 N sodium hydroxide solution with alizarin S as the indicator. The reaction is given by the following equation:



**Procedure.** To 2 ml. of the solution containing magnesium, add 2.2 g. of solid potassium iodide, and when this is dissolved add 0.9 ml. of a solution containing 15 g. of potassium iodide in 30 ml. of a cold saturated solution of hexamethylenetetramine. Stir well and cool in ice for at least 30 minutes. Filter through a Schott 12Q3 or 12Q4 microfilter, wash with acetone saturated with the complex, and finally with chloroform which is also saturated with the complex. Dissolve in water, and add 2 ml. of 0.05 N sulfuric acid. Heat on a water bath for 10 minutes, and then titrate with 0.01 N sodium hydroxide solution. One ml. of 0.01 N  $\text{H}_2\text{SO}_4$  is equivalent to 0.0304 mg. of magnesium.

High results are obtained when calcium is present in quantities greater than 0.2 mg. per ml. In most biological liquids, however, the calcium concentration is below this limit, and consequently does not interfere. Phosphates cause low results and must be removed.

Isibasi<sup>39</sup> has determined the proper heating temperature for magnesium complexes with hexamethylenetetramine which are given in Table 21:

TABLE 21.

Metal	Determined As	Proper Heating Temperature
Magnesium	$[\text{Fe}(\text{CN})_6\text{CaMg}]_3 \cdot 4(\text{CH}_2)_6\text{N}_4 \cdot 40\text{H}_2\text{O}$	$< 25^\circ$
Magnesium	$\text{MgI}_2 \cdot 10\text{H}_2\text{O} \cdot 2(\text{CN})_6\text{N}_4$	$< 40^\circ$

Alten and co-workers<sup>40</sup> have used hexamethylenetetramine for the removal of calcium and magnesium in the colorimetric determination of aluminum with 8-hydroxyquinoline.

**Determination of beryllium.** Akiyama<sup>41,42</sup> has used hexamethylenetetramine for the precipitation of beryllium:

**Procedure.** To 25 ml. of a solution of beryllium nitrate, containing 0.05 g. of  $\text{BeO}$ , add 15 ml. of molar hexamethylenetetramine and 2 g. of ammonium nitrate. Dilute to 70-100 ml. and heat for 40 minutes. Filter, wash the precipitate with a 0.5 per cent solution of ammonium nitrate and hexamethylenetetramine, and dry at  $107\text{--}110^\circ \text{C.}$  for 2.5 hours. Ignite and weigh as  $\text{BeO}$ .

This method appears to be useful in the presence of considerable quantities of aluminum.

**Detection of lithium.** Lithium may be detected by means of the shiny yellow crystals which form when a solution of a lithium salt is treated with hexamethylenetetramine and a solution of potassium ferricyanide.<sup>27,43-45</sup>

**Procedure.** Treat 1 drop of the solution to be tested with a drop of a 15 per cent solution of hexamethylenetetramine, and add 1 drop of a 15 per cent solution of potassium ferricyanide. The formation of shiny yellow octahedrons, which are visible under the microscope, reveals the presence of lithium. By means of this reaction 0.06% of lithium can be detected at a concentration of 1:50,000.

**Microchemical detection of the metals.** In addition to the various microchemical reactions which have been described in the preceding sections, hexamethylenetetramine reacts with various cations, and in the presence of various salts to form crystalline compounds which may be used for the detection of many ions. Vivario and Wagenaar<sup>46</sup> and Korenman<sup>47</sup> have studied the reactions of hexamethylenetetramine with various salts and report that characteristic insoluble crystals are formed with platinum, palladium, iridium, osmium, silver, mercury, antimony, tin and magnesium. Singleton<sup>48</sup> and Whitmore and Schneider<sup>49</sup> have used hexamethylenetetramine for the microchemical detection of metals of the platinum group. The results obtained by adding a solid fragment of hexamethylenetetramine to a 1 per cent solution of various platinum metal salts are given in Table 22:

TABLE 22.—REACTIONS OF HEXAMETHYLENETETRAMINE WITH PLATINUM SALTS

Test Material	Description
$\text{RuCl}_3$	A dense brown amorphous precipitate forms around test-particle immediately.
$\text{RhCl}_3$	No apparent reaction.
$\text{PdCl}_2$	A very dense yellow precipitate forms around the test particle. The precipitate is so dense that no crystalline forms can be distinguished.
$\text{Na}_2\text{OsCl}_6$	A dense granular precipitate forms immediately around the reagent particle. At the edge of this precipitate a great many small, but well defined, bright-yellow octahedra develop.
$\text{IrCl}_3$	A dark amorphous precipitate is formed immediately around the reagent particle. This precipitate gradually extends over the entire drop and at the edge develops into deep red octahedra. Most of these crystals are poorly formed.
$\text{H}_2\text{PtCl}_6$	A very dense yellow precipitate forms at once. On close examination it is seen that this precipitate is made up of very tiny yellow octahedra. At the circumference these are quite well developed though very small.
$\text{AuCl}_3$	A very dense yellow precipitate surrounds the test particle immediately. Around the circumference of this precipitate there extends into the drop an entangled network of straight, long, very slender, yellow crystals.

Hexamethylenetetramine may also be used with potassium iodide for the microdetection of antimony, copper, bismuth, tin and cadmium.<sup>46,50,51,59-61</sup> In general, the reactions are made more sensitive by using potassium iodide. Both bismuth and antimony form compounds with potassium iodide and hexamethylenetetramine, but the bismuth reaction never yields crystals which are capable of polarizing light, and in this way they may be distinguished from those formed with antimony. Potassium bromide may be used in place of potassium iodide in these reactions.

The addition of hexamethylenetetramine and ammonium thiocyanate to solutions containing various cations results in the formation of crystalline compounds which can be used for the microchemical detection of copper, zinc, iron, vanadium, indium and molybdenum.<sup>51,52,58</sup> The following results are reported by Martini:<sup>52</sup>

Salt	Description
Cupric chloride	Light yellow tablets
Zinc chloride	Thin white needles
Ferrous chloride	Light red crystals
Vanadyl chloride	Light red hexagons
Indium chloride	Reddish-white prisms
Ammonium molybdate	Red hexagonal crystals or yellow prisms

Ray and Sarkar<sup>27</sup> have studied the microchemical reactions of hexamethylenetetramine with various metals and have proposed the use of a number of

reagents for the detection of magnesium, calcium, lithium, molybdenum, silver, manganese, nickel and cobalt. Their results are given in Table 23.

TABLE 23.—REACTIONS OF CATIONS WITH HEXAMETHYLENETETRAMINE.

Metal	Reagent	Description	Sensitivity
	Reagent = $(\text{CH}_2)_6\text{N}_4$		
Magnesium	$\text{K}_3\text{Fe}(\text{CN})_6$ + reagent	Yellow crystals	0.0005 $\gamma$
Magnesium	$\text{K}_4\text{Fe}(\text{CN})_6$ + reagent	Cream	0.002 $\gamma$
Magnesium	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ + reagent	Rose-red	0.008 $\gamma$
Magnesium	$\text{K}_3\text{Co}(\text{S}_2\text{O}_8)(\text{CN})_6$ + reagent	Yellow	0.008 $\gamma$
Magnesium	$\text{Na}_2\text{S}_2\text{O}_8$ + reagent	Colorless	0.004 $\gamma$
Calcium	$\text{K}_3\text{Fe}(\text{CN})_6$ + reagent	Yellow	0.008 $\gamma$
Lithium	$\text{K}_3\text{Fe}(\text{CN})_6$ + reagent	Yellow	0.065 $\gamma$
Lithium	$\text{K}_4\text{Fe}(\text{CN})_6$ + reagent	Cream	0.065 $\gamma$
Molybdenum	$\text{H}_2\text{SO}_4$ + reagent	Colorless	0.065 $\gamma$
Silver	$\text{Na}_2\text{S}_2\text{O}_8$ + reagent	Colorless	0.065 $\gamma$
Manganese	$\text{Na}_2\text{S}_2\text{O}_8$ + reagent	Colorless	0.02 $\gamma$
Nickel	$\text{Na}_2\text{S}_2\text{O}_8$ + reagent	Light green	0.15 $\gamma$
Cobalt	$\text{Na}_2\text{S}_2\text{O}_8$ + reagent	Light red	0.02 $\gamma$
Cobalt	$\text{NH}_4\text{SCN}$ + reagent		0.15 $\gamma$
Mercury	$\text{HI}$ + reagent	Light yellow	0.035 $\gamma$

**Detection of complex cyanides.** The reaction obtained when a ferricyanide is mixed with hexamethylenetetramine and a lithium salt is used as the basis for a microchemical test for ferricyanides:<sup>53</sup>

**Procedure.** Evaporate a few drops of the solution to be tested to dryness by warming on a glass slide, and then add a drop of a reagent containing equal parts of 15 per cent lithium chloride solution and a solution of hexamethylenetetramine. The formation of a yellow crystalline precipitate can be accelerated by rubbing the mixture with a glass rod. Under the microscope intense yellow octahedral and dendritic crystals appear in the form of 4- and 6-pointed stars. This reaction is sensitive to 0.05 $\gamma$  of ferricyanide at a dilution of 1:40,000.

Ferrocyanides give a similar reaction, except that colorless thin platelettes, rosettes and spherical crystals are obtained. The sensitivity of this reaction is 0.06 $\gamma$  of ferrocyanides at a limiting concentration of 1:30,000. Both ions can be detected when present in the same solution.

Cyanates and carbonates form colorless, non-characteristic precipitates with the reagent, but these do not interfere with the test for the complex cyanide. Hexamethylenetetramine gives no precipitate with chloride, bromide, iodide, thiocyanate, dichromate, tetraborate, acetate, nitrate, nitrite, sulfate, thiosulfate, chlorate and permanganate.

**Determination of tellurium.** Tellurium may be precipitated as tellurium dioxide,  $\text{TeO}_2$ , by the following procedure proposed by Clauder:<sup>54</sup>

**Procedure.** To an acid solution containing not more than 0.2 g. of tellurium, calculated as the dioxide, add ammonium hydroxide until a slight permanent precipitate is formed, and then add 10 ml. of N hydrochloric acid and dilute to 100 ml. At least 1 g. of ammonium chloride should be present. Heat to boiling, and to the hot solution add dropwise 10 ml. of a 20 per cent solution of hexamethylenetetramine. Allow to stand overnight and filter through a glass filter crucible. Wash the precipitate with 50 ml. of water, and finally with 5 ml. of alcohol. Dry at 132° C. and weigh as  $\text{TeO}_2$ .

Since selenium is not precipitated under the conditions prevailing in the above procedure, this method provides a means of separating selenium and tellurium.

Hecht and John<sup>55</sup> have used the above reaction for the microdetermination of from 0.1-5.0 mg. of tellurium.

**Procedure.** Evaporate to dryness 1-10 ml. of the solution containing 0.5-5.0 mg. tellurium. Take up the residue in 0.1-0.2 ml. of concentrated hydrochloric acid and with cooling mix with an equal quantity of concentrated ammonia. Add a few drops of water to complete solution, and then add 1:1 ammonium hydroxide to the appearance of a permanent milky turbidity. Acidify with 0.1-0.4 ml. of 1 N hydrochloric acid, according to the quantity of tellurium present, and add a few crystals of ammonium chloride. Now dilute with water according to the quantity of tellurium as follows:

Quantity of Te mg.	Volume ml.
0.5	0.7
1.0	1.3
1.5	2.0
2.5-5.0	3.5

Heat for 2 minutes on a boiling water bath and then add a volume of 20 per cent hexamethylenetetramine solution, determined by the amount of tellurium present as follows:

Quantity of Te mg.	Volume of 20% Hexa Solution ml.
0.5	0.12
1.0	0.24
1.5	0.35
2.5-5.0	0.6-0.75

First add a few drops of the reagent, swirl the mixture and allow to come to boiling, and then continue to add the hexamethylenetetramine in small quantities until the indicated volume has been used. Boil for 1-2 minutes, and then allow

to stand 2 hours. Filter with suction, and wash the precipitate with 0.3-0.5 ml. cold water and then twice with 0.3 ml. 96 per cent alcohol. Dry at 105° C. and weigh as  $\text{TeO}_2$ .

Selenium is determined in the filtrate by reducing with sulfur dioxide in an acid solution.

**Detection of bromide and iodide.** Hexamethylenetetramine may be used for the detection of bromide and iodide in the presence of other ions which are precipitated by silver nitrate. Hexamethylenetetramine forms complexes with silver chloride and silver bromide which require but very little ammonium hydroxide to dissolve them. The addition of the silver chloride complex to a solution of a bromide or iodide results in the formation of a precipitate. The addition of a slightly ammoniacal and saturated solution of chloride increases the sensitivity of the silver chloride or silver bromide complex:<sup>56</sup>

**Reagent.** Dissolve 0.1 mole of freshly prepared and washed silver chloride in a mixture of 300 ml. of cold saturated hexamethylenetetramine solution and 300 ml. of cold saturated sodium chloride solution. Add sufficient ammonium hydroxide to keep the complex in solution, and dilute with water to 1 liter. A similar reagent prepared by using silver bromide instead of silver chloride, and without the sodium chloride, is excellent for the detection of iodides in the presence of chlorides and bromides:

**Procedure.** Add 1 drop of the reagent to 1 ml. of the solution to be tested. A precipitate forms when only 0.01 per cent of the halogen is present in the solution to be tested.

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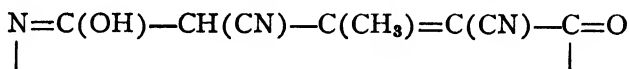
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### $\gamma$ -METHYLDICYANODIHYDROXYHYDROPYRIDINE

$C_8H_5O_2N_3$

Mol. Wt. 175.12

Beil. Ref. XXII, 278 (569)



**Use:** Detection of potassium and sodium.

$\gamma$ -Methyldicyanodihydroxyhydropyridine crystallizes as leaves with 2.5 molecules of water. The hydrate melts at  $244^\circ\text{C.}$ , and the anhydrous compound melts at  $250\text{--}252^\circ\text{C.}$  It is readily soluble in water and in alcohol.

**Preparation:**  $\gamma$ -Methyldicyanodihydroxyhydropyridine is prepared by the reaction of a cold mixture of cyanacetic ester, ammonia, and acetaldehyde.<sup>1,2</sup>

**Detection of sodium and potassium.** Piccinini<sup>2</sup> has used  $\gamma$ -methyldicyanodihydroxyhydropyridine as a sensitive reagent for the detection of sodium and potassium. The sodium and potassium salts of this reagent are only slightly soluble in water, and are formed by the addition of the reagent to aqueous solutions containing sodium and potassium ions. This reagent can be used only in a systematic scheme of analysis, after the removal of other cations, or in solutions which are known to contain no alkaline earths, ammonium salts, or salts of the heavy metals. Despite the fact that this reagent is not characteristic of potassium or sodium, it is capable of precipitating 0.6-0.7 mg. of potassium in 1 ml. of solution. Moreover, the sensitivity of this reaction is not diminished in the presence even of considerable quantities of the mineral acids. As much as 2 per cent hydrochloric acid, 3 per cent nitric acid, and 5 per cent sulfuric acid may be present while making this test. The microscopic appearance of the crystals of the sodium and potassium salts is useful in distinguishing these compounds. The test is carried out as follows:

**Procedure.** The solution to be analyzed must contain none of the metals of the first four analytical groups, and ammonium salts must be removed by evaporating to dryness and heating until the ammonium salt is decomposed. Take up the residue with a few drops of water, and treat 1 or 2 drops of this solution with a few drops of a 2.5 per cent aqueous solution of  $\gamma$ -methyldicyanodihydroxyhydropyridine. A crystalline precipitate forms in the presence of sodium or potassium. By examining the mixture under a microscope, as little as 0.6 mg. of potassium can be detected in the presence of a large quantity of sodium.

Even though the sodium salt is also precipitated, potassium may be detected by taking 1 or 2 drops of the solution to be tested, diluting with 1 ml. of 80-90 per cent alcohol and treating with a few drops of the reagent. Under these conditions, the sodium salt is not precipitated, even though the solution contains



a considerable quantity of sodium, while the potassium salt precipitates immediately. In this fashion, it is possible to detect 0.3 mg. of potassium.

Lithium is not precipitated by the reagent, even from concentrated solutions of lithium salts, and in the presence of 90 per cent alcohol.

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## NITRON

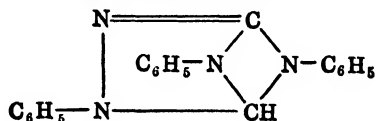
Synonym: 1,4-Diphenyl-3,5-endanilodihydrotriazol

$C_{20}H_{16}N_4$

Mol. Wt. 312.36 Beil. Ref. XXVI, 349 (110).

**Use:** Detection of nitrate, perchlorate and rhenium.

Determination of boron, nitrate, perchlorate, rhenium and tungsten.



Nitron consists of yellow leaflets, or occurs as a yellow powder. It melts at about 189° C. with decomposition. It is insoluble in water, soluble in alcohol, benzene, acetone, chloroform, ethyl acetate, and is slightly soluble in ether. The alcoholic solution undergoes a partial decomposition, which is detected by a red color, and for this reason the solution should be protected from light. The compound is a rather strong base.

**Preparation.** *Triphenylaminoguanidine*: Mix 20 g. of thiocarbanilide and 500 ml. of dry benzene, and heat to boiling under reflux. While boiling, add lead oxide or mercuric oxide in small portions as long as a dark color results. Filter off the precipitate of the metallic sulfide, and mix the still hot filtrate with 10 g. of phenylhydrazine, and at once distill to a volume of 50 ml. Allow the mixture to cool and add a little gasoline. The mixture solidifies to a crystalline mass. Filter with suction and wash with a little ether.

**Nitron:** Heat the above compound with twice its quantity of 90 per cent formic acid in a tube to a temperature of 175° C. for 2 hours. Then mix the product with 10 times as much water, filter, and precipitate the base as a yellow compound with ammonium hydroxide. Immediately take up with chloroform and dry the chloroform solution with potassium carbonate. Concentrate the chloroform solution to about one-fourth of its volume, and add 1 drop of petroleum ether and allow to cool. Collect the crystals which form and purify by recrystallizing from alcohol.<sup>1,2,3</sup>

**Detection and determination of nitric acid.** Nitron forms with nitric acid a fairly insoluble crystalline nitrate,  $C_{20}H_{16}N_4 \cdot HNO_3$ , which is used for the separation and the quantitative estimation of this acid. This procedure was originally proposed by Busch<sup>2-5</sup> and was later studied by Gutbier<sup>6,7</sup> and others.<sup>8-11</sup>

The solubility of nitron nitrate in a slightly acidified aqueous solution has been reported as 9.9 mg. in 100 ml. of water at room temperature, but according to the investigations of Winkler<sup>11</sup> this value is too low. He reports that at 20° C., 37.1 mg. of nitron nitrate dissolves in 100 ml. of water after standing 24 hours. If, on the other hand, the solution is saturated at a higher temperature and allowed to cool to 20° C., and then allowed to stand 24 hours at this temperature, 53.1 mg. of nitron nitrate dissolve in 100 ml. of water. At 0° C. the solubility is 21.13 or 33.7 mg. per 100 ml., depending on the method used. It is fortunate, however, that the solubility is greatly reduced in the presence of nitron acetate. For example, if 10 ml. of nitron acetate solution (see procedure) is added to 100 ml. of nitron nitrate solution, saturated at 17.5° C., the solubility after 24 hours is found to be only 2.0 mg. of nitron nitrate.

**Reagent.** Dissolve 10 g. of nitron in 100 ml. of 0.1 N acetic acid. Filter the solution through a porous glass filter crucible, and store the filtrate in a dark bottle.

**Procedure.** Dissolve the material to be analyzed, which should contain the equivalent of not more than 0.1 g. of nitric acid, in 80-100 ml. of water containing 1 ml. of glacial acetic acid. Heat almost to boiling, and add at one time 10-12 ml. of the nitron acetate solution. Allow the mixture to stand for 24 hours in a dark place, and then filter through a Gooch crucible. Transfer the precipitate to the crucible with the mother liquor. Allow to stand for a time until most of the pale yellow solution has drained from the precipitate, and then wash with 10-12 ml. of ice water, added in small portions. Allow the precipitate to drain after each washing. Dry at 110° C. for 2 hours and weigh as nitron nitrate. The factor for nitrate is 0.1679.

Despite the fact that nitron nitrate is appreciably soluble in slightly acidified solutions, the results of the nitron determination are rarely low. This is probably due to the fact that the precipitate contains some occluded nitron acetate which compensates for the errors arising from incomplete precipitation.

According to Winkler<sup>11</sup> the quantity of ice water originally recommended for the washing is insufficient, and he suggested the use of a saturated solution of nitron nitrate as the wash liquid.

**Procedure.** The neutral solution to be determined should have a volume of about 100 ml., and should contain 0.01-0.05 g. of nitrate. Acidify this solution with 1 ml. of acetic acid, warm to 60-70° C. and add 10 ml. of completely clear reagent solution. Allow to stand 24 hours in the dark, and collect the precipitate on a small pad of cotton contained in a funnel. Wash with 50 ml. of a saturated solution of nitron nitrate, and quickly remove the last portion of the wash solution with suction. Dry the precipitate 2-3 hours at 100° C. The factor for nitrate is 0.1679.

The following procedure has been used by Collins:<sup>18</sup>

**Reagent.** In an atmosphere of coal gas, dissolve 10 g. of nitron base in 100 ml. of 5 per cent acetic acid with gentle warming, and then filter quickly into a dark glass bottle in which the air has been replaced with coal gas.

**Procedure.** Heat just to boiling 80-100 ml. of a solution containing not more than 0.09 g. of  $N_2O_5$ . Acidify with 2-3 drops of dilute sulfuric acid, and add 10 ml. of the nitron reagent. Allow to cool, and immerse the flask in ice-cold water for 1-2 hours. Transfer the precipitate immediately to a tared Gooch crucible. Wash 3-4 times with 3 ml. of ice-cold water, draining after each washing, and dry at 105-10° C. and weigh.

About 0.45 per cent of the weight of nitron nitrate is dissolved by 10 ml. of the ice-cold water which is used in washing the precipitate. Magnesium sulfate and potassium sulfate do not interfere. Collins<sup>13</sup> reports that in the determination of nitrate in fertilizer, the error obtained with the above method was about 0.81 per cent; with lead nitrate, about 0.47 per cent; and with calcium nitrate, 1.7 per cent. The determination cannot be carried out in the presence of bromide, iodide, nitrite, chromate, chlorate, perchlorate, perrhenate, thiocyanate, ferrocyanide, ferricyanide, oxalate and picrate, since the corresponding nitron salts are more or less insoluble. Table 24 gives the solubility in grams of some nitron salts in 100 ml. of very dilute acid solutions.

TABLE 24.—SOLUBILITY OF NITRON SALTS

Salt	Solubility
Nitrate .....	0.0099
Perchlorate .....	0.008
Iodide .....	0.017
Thiocyanate .....	0.04
Chromate .....	0.06
Chlorate .....	0.12
Nitrite .....	0.19
Bromide .....	0.61

Hydrobromic acid can be decomposed by adding chlorine water dropwise to the boiling solution until the yellow color of bromine disappears. Hydroiodic acid is removed by adding an excess of potassium iodate to the neutral solution and boiling off the iodine. Nitrous acid is removed by the addition of powdered hydrazine sulfate to the concentrated solution, and chromic acid is also reduced with hydrazine sulfate.<sup>16</sup>

The nitron method gives good results in the presence of sulfates and iodates, but if large quantities of chlorides are present, a correction factor must be applied. The correction factor is determined by an analysis of pure nitric acid containing the same weight of chloride.<sup>11</sup> Since the errors caused by chloride are fairly constant, corrections based on the weight of the precipitate may be applied. These corrections are given in Table 25.

Pooth<sup>14</sup> has studied the effect of hydrochloric acid upon the precipitation of nitron nitrate, and has reported that the upper limit for the complete precipitation of nitrate is 100 ml. of N hydrochloric acid for each 0.1 g. of nitrate.

The nitron method is not affected by the presence of 1 per cent of magnesium

sulfate, calcium chloride, aluminum sulfate, ammonium sulfate, dipotassium hydrogen phosphate or magnesium chloride, 2 per cent of tartaric or citric acid, or 10 per cent of saccharose or glucose, or 0.2 per cent peptone. Two per cent of dextrin or as little as 0.25 per cent of gelatine interferes with the formation of the precipitate and causes low results. The presence of oxalic acid causes irregularly high results, and chloric acid is precipitated quantitatively if the concentration exceeds 3 parts per thousand.<sup>12</sup>

TABLE 25.

Weight of Precipitate	Chloride in 100 ml.			
	0.0 g.	0.1 g.	0.3 g.	0.5 g.
0.30 g.	+0.4 mg.	—2.0 mg.	—4.4 mg.	—6.8 mg.
0.20 g.	+0.8 mg.	—1.2 mg.	—3.0 mg.	—4.8 mg.
0.10 g.	+1.2 mg.	—0.2 mg.	—1.5 mg.	—2.8 mg.
0.05 g.	+1.4 mg.	+0.2 mg.	—0.8 mg.	—1.8 mg.

Vasilev<sup>15</sup> has determined nitrate in the presence of various cations and reports that good results can be obtained in determining nitrate as the potassium, ammonium, magnesium, zinc, cadmium, manganese, aluminum and uranyl nitrates. In precipitating nitrates from solutions of various salts, and under varying conditions, there appears to be no serious entrainment of either the cation or the precipitant.<sup>16</sup>

The determination of nitric acid with nitron has been applied to many practical forms of analysis. Among the various materials which have been analyzed in this manner are meats and meat extracts,<sup>17-19</sup> plant tissue,<sup>20</sup> Chili saltpeter,<sup>21</sup> explosives<sup>22</sup> and sulfuric acid.<sup>23</sup>

Nitrate may also be detected or determined by means of nitron formate, or *fornitral*, which contains 2 moles of formic acid united with 1 mole of nitron. This compound is very soluble in water with a very distinct acid reaction, and a 10 per cent solution of this reagent is more stable than the nitron solution which it is proposed to replace.<sup>24-26</sup> The addition of 5-6 drops of *fornitral* to 1 ml. of cold water containing 0.03 mg. of nitric acid causes an immediate precipitation, and a precipitate is obtained after 5 hours with as little as 0.0075 mg. of nitric acid. Various other acids form slightly soluble salts with *fornitral*. The solubility of these compounds is given in Table 26. The numbers in the second column represent the number of ml. of water required to dissolve 1 g. of the salt.

The following procedure is used for the determination of nitrate.

**Procedure.** To a solution containing 0.1 g. of nitric acid per 100 ml. add 10 drops of dilute sulfuric acid, heat nearly to boiling, and add 10 ml. of a 10 per cent solution of *fornitral*. Cool, allow to stand in ice for 2 hours, filter through a Gooch crucible and wash with three 4 ml. portions of cold water. Dry at

100-110° C. for 1 hour and weigh. The precipitate contains 16.8 per cent of nitric acid.

TABLE 26.

Salt	Number of ml. of Water Required to Dissolve 1 g. of Salt
Bromide .....	300
Chlorate .....	400
Nitrite .....	4,000
Dichromate .....	6,000
Thiocyanate .....	15,000
Perchlorate .....	50,000
Nitrate .....	60,000 at 15° C.
Nitrate .....	80,000 at 0° C.

Fornitral is particularly well suited for the determination of nitrate in soils, plant extracts, culture media, fertilizers and effluents. The process is not affected by the presence of tartaric acid, citric acid, sucrose, glucose, urea, asparagin, aspartic acid, alkali, phosphate, and salts of magnesium, calcium, lead and aluminum. Oxalic acid, if present in appreciable quantities, may cause high results. It has been used for the determination of nitrate in ammonium nitrate melts.<sup>45</sup>

In the use of nitron or nitron formate for the estimation of nitrates, if a not too concentrated solution is diluted with a saturated solution of nitron nitrate and the precipitate of nitron nitrate is washed with this same saturated solution, the procedure can be carried out at room temperature and gives almost theoretical results.<sup>24</sup>

**Procedure.** To 2 ml. of the solution to be analyzed add 2 ml. of a saturated nitron nitrate solution and heat to boiling. Add 3 drops of sulfuric acid, and 2 ml. of 10 per cent fornitral solution. Allow to stand for 24 hours in diffused light and filter. Wash with three 4-ml. portions of a saturated nitron nitrate solution and dry at 100-110° C. for 1 hour. The fornitral solution should be filtered each time before use.

With approximately 1 mg. of nitrate, the error obtained using this procedure does not exceed 3 per cent. The original concentration of the nitrate should not exceed 0.5 g. per liter.

**Detection and determination of rhenium.** In a slightly acid solution containing a soluble perrhenate, nitron acetate precipitates insoluble nitron perrhenate. Approximately 17-18 mg. of this salt dissolves in 100 ml. of pure water, but in the presence of 0.3-0.5 per cent nitron acetate the precipitate is practically insoluble. The formation of this compound may be used for the detection and determination of rhenium. Rhenium is usually detected microscopically by means of the characteristic crystals of nitron perrhenate,<sup>27,28</sup> but Kronman and Bibikova<sup>29,43,44</sup> have proposed an interesting modification of this reaction. This test is carried out as follows:

**Procedure.** Place a drop of a nitric acid solution containing potassium perrhenate on a glass slide and treat with a drop of nitron acetate and a drop of sodium sulfide solution. To this mixture, which contains crystals of nitron nitrate and nitron perrhenate, add 1 drop of a hot 10 per cent gelatin solution. Allow the drop to solidify, and then place upon the mixture a drop of a titanium trichloride solution. This gradually diffuses through the gelatin, and after about 1 hour the nitron perrhenate crystals become dyed brownish-yellow with rhenium disulfide,  $\text{ReS}_2$ .

Wenger and Duckert<sup>30</sup> have recently studied the various methods for detecting rhenium, and do not recommend the use of nitron, since this reagent gives similar reactions with too many other ions.

Nitron perrhenate is sufficiently insoluble to make possible the use of nitron as a quantitative precipitant for rhenium.<sup>31-35</sup> The following procedure has been proposed by Geilman and Voigt:<sup>33</sup>

**Procedure.** To the neutral solution containing not more than 0.1 g. of rhenium as the perrhenate, add sufficient hot water to make the volume 50 ml., and add 1 ml. of 2 N sulfuric acid. Heat to 80° C. and add sufficient 5 per cent nitron acetate so that the solution will contain 0.3-0.4 per cent of the free reagent after precipitating all the rhenium. Cool the mixture for 2 hours in ice water with frequent and vigorous stirring. Filter and wash with 10-20 ml. of an ice-cold 0.3 per cent nitron solution divided into 3-5 ml. portions, and suck dry after each washing. The precipitate may be washed 2-3 times with 2-3-ml. portions of an ice-cold saturated aqueous solution of nitron perrhenate. Finally dry the washed precipitate for 2 hours at 110° C. and weigh as nitron perrhenate. The factor for rhenium is 0.3306.

The following procedure may be used to determine rhenium after preliminary precipitation as rhenium sulfide:<sup>34,43</sup>

**Procedure.** Make the solution 3.6-4.2 N in hydrochloric acid, heat, and pass hydrogen sulfide through the mixture for 2-2.5 hours while allowing the solution to cool. Wash the precipitate with 0.3 N hydrochloric acid which is saturated with hydrogen sulfide. Add 3-5 ml. of 5 per cent sodium hydroxide solution to the sulfide precipitate, and then add 2-3 ml. of hydrogen peroxide, which converts the sulfide to sulfate and the rhenium to the perrhenate. Boil to remove the excess peroxide and neutralize with 2 N sulfuric acid. Precipitate the hot solution with nitron acetate as described above.

Molybdenum, which may interfere with the rhenium determination, may be removed with 8-hydroxyquinoline.<sup>31</sup>

**Determination of perchlorate.** Perchlorates may be detected or determined by the formation of an insoluble salt with nitron. The following procedure is due to Loebich:<sup>36</sup>

**Reagent.** Dissolve 10 g. of nitron in 10 g. of glacial acetic acid and add 85 ml. of water.

**Procedure.** Dissolve the material containing about 100 mg. of the perchlorate ion in 60 ml. of water, and add 1 ml. of 2 N sulfuric acid. Heat until the solution begins to boil and then remove the flame. For each 100 mg. of perchlorate ion, add 10 ml. of the nitron solution. Nitron perchlorate immediately separates as a crystalline solid. Cool the mixture in ice for 2-3 hours and filter. Wash rapidly with 10 ml. of ice water in 6-7 portions and dry at 110° C. Weigh as nitron perchlorate. The factor for  $\text{KClO}_4$  is 0.3358.

Nitrates, chlorates and perchlorates yield characteristic precipitates with nitron. By treating a mixture of these salts with Devarda's alloy (59 parts aluminum, 39 parts copper and 2 parts zinc) in an alkaline solution the chlorate and the nitrate are reduced while the perchlorate remains unaffected. This behavior makes possible the determination of perchlorates in mixtures containing chlorates and nitrates. Vurtheim<sup>87</sup> has made use of this principle in determining perchlorate in Chili saltpeter.

**Procedure.** Dissolve 50 g. of the carefully ground sample of Chili saltpeter in 500 ml. of water and filter. Mix 10 ml. of the filtrate in a 100 ml. flask with 20 ml. of water and 2 ml. of 96 per cent alcohol. Place the flask and contents in a vessel filled with cold water, and reduce the mixture with 2.5 g. of Devarda's alloy and 20 ml. of 30 per cent sodium hydroxide. Best results are obtained by adding at first about one-half quantities of the alloy and sodium hydroxide, and then adding the rest after the first vigorous evolution of gas has ceased. Allow the mixture to stand for about one-half hour after the reaction appears to be complete. Then add 15 ml. of concentrated acetic acid, dilute to exactly 100 ml., and shake gently. Filter and treat 25 ml. of the filtrate (this is equivalent to 0.25 g. of saltpeter) with 2 ml. of 10 per cent acetic acid and 10 ml. of 2 per cent nitron in dilute acetic acid. Allow the mixture to stand for 24 hours, filter into a weighed Gooch crucible, wash with 10 ml. of water, dry at 105° C. for 1 hour and weigh. Obtain the per cent of  $\text{KClO}_4$  in the original sample by multiplying the weight of the precipitate by 1.357.

Results obtained with this method agree very closely with those employing other methods.

**Determination of tungsten.** Gutbier and Weise<sup>88</sup> have used nitron for the separation and determination of tungstic acid or soluble tungstates.

**Procedure.** The weighed sample of tungstic acid is moistened with a little water and then dissolved with the aid of heat in the smallest possible quantity of concentrated sodium hydroxide. In analyzing an alkali tungstate, simply dissolve in water and proceed as follows:

Dilute the clear solution of the alkali tungstate or tungstic acid to about 150 ml. with boiling water. Acidify with acetic acid and heat to boiling. Then add slowly with vigorous stirring an excess of a 10 per cent solution of nitron in 5 per cent acetic acid. Cool, allow to stand until the supernatant liquid is clear, and then filter. Wash the precipitate with a mixture of 4 ml. of the precipitant and 96 ml. of water until the filtrate is free from alkali. Heat the

precipitate in a platinum crucible, and ignite at about 800° C. to constant weight. Weigh as  $\text{WO}_3$ .

Care must be taken that the solution is not boiled after adding the precipitant, since under these conditions the supernatant liquid remains turbid and filtration is very slow.

Excellent results are reported using tungstic oxide. The precipitate can not be weighed directly, since it decomposes fairly rapidly. The white precipitate soon becomes yellow, apparently due to the presence of traces of ammonia in air.

**Determination of boron.** Lange<sup>39</sup> and others<sup>40,41</sup> have studied the reactions of nitron with a number of boron compounds and report that precipitates are formed with fluoborates, difluorophosphates, and fluorosulfonates. The composition of the difluorophosphate precipitate is  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{H}[\text{PO}_2\text{F}_2]$ . Nitron fluorosulfonate has the composition  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{HSO}_3\text{F}$ , and dissolves to the extent of only 0.0318 g. in 100 ml. of solution. The compound formed when nitron reacts with fluoroboric acid is  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{HBF}_4$ .

Berkovich and Kulyashev<sup>42</sup> have used nitron for the determination of boron in Dow Welding Flux. This depends upon the precipitation of the boron as nitron fluoroborate,  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{HBF}_4$ .

**Procedure.** Dissolve 5 g. of the flux in 100 ml. of water and neutralize a 10 ml. aliquot with ammonium hydroxide. To this add 10 ml. of a solution of 1.3 parts of nitron in 10 ml. of 5 per cent acetic acid at 0° C. Allow to stand for 10 minutes and filter the precipitate. Wash with very dilute acetic acid and dry at 105° C. to constant weight.

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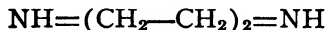
## PIPERAZINE

Synonym: Diethylenediamine, piperazidine, hexahydropyrazine

$C_4H_{10}N_2$

Mol. Wt. 86.12

Beil. Ref. XXIII, 4.



**Use:** Detection of antimony, bismuth, gold, molybdenum, tin, tungsten and vanadium.

Separation of manganese from iron and aluminum.

Piperazine consists of colorless, hygroscopic, volatile crystals. It is a strong base, and absorbs carbon dioxide from the air. It melts at 104° C. when anhydrous, and boils at 145-146° C. It is very soluble in water and glycerol, but is less soluble in alcohol, and is insoluble in ether.

The reagent crystallizes from water as colorless crystals containing 6 molecules of water of hydration. This compound, which is the usual article of commerce, is called piperazine hydrate, and melts at 44° C., and boils at 125-130° C.

**Preparation:** Mix thoroughly 958 g. of ethylene bromide, 527 g. of aniline and 575 g. of anhydrous sodium carbonate, and boil gently 5-6 hours under

reflux and with stirring. Extract the warm melt with hot water to remove sodium bromide from the diphenylpiperazine.

Dry and powder 547 g. of the diphenylpiperazine and suspend it in 2200 ml. of cold concentrated hydrochloric acid. Stir mechanically, and slowly add through a tube extending to the bottom of the acid a saturated solution containing 438 g. of sodium nitrite. Cool during the addition of the nitrite. Filter the resulting product with suction and wash once with cold water.

Add the moist material to a 40 per cent solution containing 1900 g. of sodium bisulfite, and warm the suspension, with stirring, to about 80° C. Filter, and make the reddish-orange filtrate strongly alkaline with sodium hydroxide, and then concentrate by distillation. Continue the distillation with superheated steam with the flask immersed in an oil bath at 160° C. Piperazine distills with steam and is collected in hydrochloric acid. Continue the distillation until all piperazine has passed over. This may be determined by a microtest of the distillate with platinic chloride, which yields characteristic yellow crystals. Picric acid may also be used for this purpose. Evaporate the aqueous distillate, which is distinctly acid with hydrochloric acid, to dryness, and then recrystallize the hydrochloride from dilute alcohol, or convert to the free base by distilling with sodium hydroxide.<sup>1-3</sup>

**Detection of antimony, bismuth, gold and tin.** A mixture of antimony chloride and sodium iodide yields microscopic yellow tablets or prisms with an acetone solution of piperazine. This reaction has been used by Martini<sup>4</sup> for the microdetection of antimony. The test is carried out by carefully adding the piperazine-acetone solution to 1 drop of the solution to be tested, to which has been added sufficient sodium iodide solution to form a yellow color. Using a similar reaction bismuth chloride yields red plates and prisms.<sup>4,5,12,14</sup>

By substituting sodium bromide for sodium iodide, gold chloride yields microscopic red plates or prisms with piperazine-acetone solution.<sup>4</sup>

Piperazine may be substituted for antipyrine in the Caille-Viel reagent for antimony and tin.<sup>6</sup>

**Detection of molybdenum, tungsten and vanadium.** Martini<sup>7</sup> has used piperazine and pyrogallol for the microdetection of molybdenum in the analysis of minerals. This procedure is based upon the formation of an orange pyrogallol-acetic acid-piperazine complex, having the following probable formula:



This compound may be identified by its characteristic crystal structure.

**Procedure.** To 1 drop of a 1 per cent ammonium molybdate solution, add pyrogallol to complete solution, and then add 1 drop of acetic acid and a concentrated solution of piperazine. The microstructure of the crystals which form is triclinic.

A similar reaction employing pyrocatechol acetate and piperazine is used for the detection of tungstate, molybdate, and vanadate. Ammonium molybdate yields an orange compound of the following probable composition.



Yellow crystals are obtained with sodium tungstate, and a black precipitate with chlorovanadic salts.<sup>8,9</sup>

The following procedure is used:

**Procedure.** To 1 drop of a 1 per cent ammonium molybdate solution on a glass slide, add a drop of a saturated solution of pyrocatechol acetate until an orange color appears, and then add a saturated solution of piperazine. With a platinum wire or a gold pen quickly remove the excess liquid, and observe the characteristic crystals which form.

Tungstates and vanadium chloride give similar reactions when treated in the above manner, and these serve for the detection of these metals. Molybdenum, tungsten and vanadium may be detected in the presence of one another.

**Detection of the platinum metals.** Whitmore and Schneider<sup>11</sup> have studied the reactions of piperazine hydrate with salts of the platinum metals in an effort to apply this reagent to the microchemical detection of these elements. Their results are given in Table 27. In their experiments, a solid fragment of piperazine hydrate was added to a 2 per cent solution of the salt.

TABLE 27.—REACTIONS OF PIPERAZINE HYDRATE WITH THE PLATINUM METALS

Test Material	Description
RuCl <sub>3</sub>	A dense, dark brown amorphous precipitate forms immediately around the test particle.
RhCl <sub>3</sub>	A dense yellowish-brown, amorphous precipitate forms around the test particle gradually.
PdCl <sub>2</sub>	A very dense, yellow, amorphous precipitate forms immediately around the test particle. At the edge of this precipitate many light-yellow, needle-shaped crystals appear. These occur singly and in clusters.
Na <sub>2</sub> OsCl <sub>6</sub>	Some quite large, bright-yellow, rectangular prisms develop gradually around the test particle. All crystals are very well formed.
IrCl <sub>4</sub>	The test particle is surrounded by a pale green zone. At the edge of this zone many small deep red octahedra appear.
H <sub>2</sub> PtCl <sub>6</sub>	The test drop is immediately surrounded by a great many pale yellow octahedra. Some short slender yellow prisms also appear.
AuCl <sub>3</sub>	A reddish-brown, amorphous precipitate forms immediately around the test particle.

**Separation of manganese from iron and aluminum.** Piperazine, in the presence of considerable ammonium sulfate or chloride, and at the boiling temperature, prevents the precipitation of manganese thereby permitting an easy and complete separation from iron and aluminum without a double precipitation. Manganese can be determined in the filtrate by precipitating as hydrated manganese dioxide with ammonium persulfate.<sup>10</sup>

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2. J. Sieber, *Ber.* **23**, 326 (1890).
3. D. S. Pratt and C. O. Young, *J. Am. Chem. Soc.* **40**, 1428-31 (1918).
4. A. Martini, *Mikrochemie.* **6**, 28-33; *C.A.* **24**, 34 (1930).
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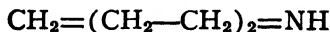
**PIPERIDINE**

Synonym: Hexahydropyridine

 $C_6H_{11}N$ 

Mol. Wt. 85.15

Beil. Ref. XX, 6.



**Use:** Detection of cobalt, gold, iridium, nickel, platinum and tin.

Determination of cerium, lanthanum, magnesium, neodymium, praseodymium, thorium and zirconium.

Piperidine is a colorless liquid which possesses the odor of pepper and ammonia. It has a caustic taste. Its sp. gr. is 0.860 and it boils at 105-106° C. It is a strong base. It is miscible with water and is soluble in alcohol, benzene and chloroform.

**Preparation:** Dissolve 20 g. of pyridine in 150 g. of absolute alcohol in a flask fitted with a reflux condenser and warm on a water-bath. Then add 75 g. of metallic sodium which has previously been cut into small pieces. As soon as the reaction slows down, or sodium alcoholate begins to separate, add alcohol and bring the reaction to an end as quickly as possible. If all the sodium has been consumed, add an equal volume of water and allow to cool. Distill with steam. Piperidine passes over with the alcohol into the distillate. Neutralize the distillate with hydrochloric acid, distill off the alcohol and evaporate to dryness. Purify the piperidine hydrochloride by recrystallizing from alcohol. The free base is obtained by treating with sodium hydroxide.<sup>1</sup>

**Detection of cobalt.** Certain amines react with sodium nitroprusside,  $Na_2[Fe(CN)_5(NO)]$ , to form salts of the general formula  $Na_2Fe(CN)_5 \cdot \text{amine}$ . Numerous primary, secondary and tertiary aliphatic amines give alkali pentacyanoaminoferroates, and these form green salts with cobalt. The piperidine derivative,  $Na_3Fe(CN)_5 \cdot C_6H_{11}N \cdot 6H_2O$ , in a 1 per cent solution is a very sensitive reagent for cobalt. In the compound produced in this reaction the three sodium atoms are replaced by cobalt. As little as 0.05% of cobalt can be detected by this method, which is particularly useful for detecting cobalt in the presence of other ions of the third analytical group.<sup>2</sup>

**Reagent.** Dissolve 3 g. of sodium nitroprusside and 1.5 g. of sodium acetate in 15 ml. of water, and add 30 ml. of methyl alcohol and 2 ml. of piperidine. Warm for a short time on a water-bath, and allow to stand in a closed vessel for one hour. Filter off the brown needles which form, and dissolve the precipitate in a little water. Shake with animal charcoal, filter and mix the filtrate with ethyl alcohol. The pure compound separates as almost white needles. Collect on a filter and wash with alcohol and ether. Prepare a stock solution of the reagent by dissolving 0.1 g. of the compound in 10 ml. of water. Add to this solution 2-3 drops of piperidine and acidify with dilute acetic acid. This solution is stable for about 1 week.

**Procedure.** Place 1 drop of the 1 per cent reagent solution on a strip of filter paper (S & S No. 601) and add a drop of neutral or weakly acid solution to be tested. If cobalt is present a grass-green spot or ring appears, according to the quantity of cobalt present. The spot cannot be removed by washing with water. By this test 0.05% of cobalt can be detected at a concentration of 1:1,000,000.

**Detection of tin.** Martini<sup>3</sup> has used piperidine for the microchemical detection of stannic tin. A concentrated solution of potassium thiocyanate and a 10 per cent solution of piperidine causes the formation of white crystals when added to a solution containing stannic tin. The sensitivity of this reaction is about 0.1% of tin.

**Detection of nickel.** The compound  $\text{Ni}[\text{C}_6\text{H}_4(\text{NH})_2]_2$  is formed by the action of *o*-phenylenediamine upon an ammoniacal solution of a nickel salt. This compound is an amorphous bluish-purple solid which is stable and insoluble in the ordinary organic solvents. It is partially soluble in piperidine with a purple coloration.<sup>4</sup>

**Detection of iridium, platinum and gold.** Whitmore and Schneider<sup>5</sup> have used piperidine hydrochloride as a microchemical reagent for the detection of iridium, platinum and gold. The results obtained by adding a little of the reagent to a 2 per cent solution of salts of these metals is given in Table 28.

TABLE 28.—REACTIONS OF PIPERIDINE HYDROCHLORIDE

Test Material	Description
$\text{IrCl}_4$	A few very small red octahedra develop at the circumference as the drop goes to dryness.
$\text{H}_2\text{PtCl}_6$	A great number of very small yellow octahedra and rectangular prisms are formed as the drop evaporates to complete dryness.
$\text{AuCl}_3$	On standing and as drop goes to dryness, quite a number of bright yellow crystals are formed. Many of these appear to be hexagonal prisms, others modified octahedra.
	The other metals give no reactions with this reagent.

**Precipitation of metals.** Jefferson<sup>8</sup> has used piperidine as a precipitant for zirconium, thorium, cerium, lanthanum, neodymium and praseodymium. Since the reagent is alkaline in reaction, these metals are precipitated as the hydroxides.

**Determination of magnesium.** Borgstrom<sup>6</sup> and Hemming<sup>7</sup> have used piperidine as a base for the precipitation of magnesium hydroxide. According to Borgstrom, piperidine is the most satisfactory of several bases which he employed for the precipitation of magnesium, although Hemming claims that guanidine gives better results.

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2. F. Feigl and R. Uzel, *Mikrochemie*. **19**, 132-43 (1936); *C.A.* **30**, 4424 (1936).
3. A. Martini, *Pub. inst. investigaciones microquim., univ. nacl. litoral.* **4**, 63-8 (1940); *C.A.* **36**, 1264 (1942).
4. F. Feigl and M. Furth, *Monatsh.* **48**, 445 (1927); *C.A.* **22**, 199 (1928).
5. W. F. Whitmore and H. Schneider, *Mikrochemie*. **17**, 279-319 (1935).
6. L. H. Borgstrom, *Hyllningsskrift tillagnad Ossian aschan.* 118-23 (1920); *C.A.* **16**, 2091 (1922).
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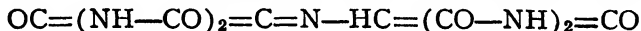
## PURPURIC ACID (Zinc Salt)

Synonym: Zinc purpurate

$C_8H_5O_6N_5$

Mol. Wt. 267.12

Beil. Ref. XXV, 499(709).



**Use:** Detection of mercury and silver.

Purpuric acid is usually employed as an analytical reagent as the ammonium salt (murexide) or as the zinc salt. The ammonium salt is an orange-red powder which is only slightly soluble in acetic acid, but dissolves in alcohol to form a yellow colored solution. It is insoluble in ether, hot benzene, chloroform and acetone. The zinc salt which is used for the detection of mercury, is prepared and used in solution without previous separation.

**Preparation:** Heat 2 g. of uric acid with 2 ml. of nitric acid ( $d = 1.38$ ) and dilute with 2 ml. of water. Continue the heating until a clear liquid is obtained and dilute to 100 ml. Boil 10 ml. of this liquid for 5 minutes with 2 g. of granulated zinc. A yellowish orange color appears in the solution due to the formation of zinc purpurate. This solution is used as the reagent.

**Detection of mercury and silver.** When a solution of a mercuric salt is treated with a small quantity of zinc purpurate solution and a few drops of sodium acetate solution, a peach-blossom colored precipitate of mercuric purpurate is formed. The formation of this precipitate may be used to detect as little as 0.4 mg. of mercuric ion per ml. of solution. Silver salts yield a violet colored precipitate with this reagent.<sup>1,2</sup>

1. G. Deniges, *Bull. soc. pharm. Bordeaux* [1] (1921); *Ann. chim. anal.* **3**, 25'-52 (1921); *C.A.* **16**, 3043 (1922).
2. G. Gutzeit, *Helv. Chim. Acta.* **12**, 716 (1929).

**URIC ACID**

Synonym: 2,6,8-Trioxypurine

 $C_5H_4O_3N_4$ 

Mol. Wt. 168.11

Beil. Ref. XXVI, 513.

**Use:** Detection of hydrogen cyanide, thallium, tungsten and zinc.

Uric acid consists of white, odorless, tasteless crystals. It decomposes on heating without melting, and the decomposition is accompanied by the evolution of hydrogen cyanide. The compound is only very slightly soluble in water and is insoluble in alcohol and ether. It dissolves in glycerol and in solutions of the alkali hydroxides and carbonates.

**Detection of zinc:** Ganassini<sup>1,2</sup> and Sensi and Testori<sup>3</sup> have used uric acid in a reaction for the detection of zinc.

**Reagent.** Dissolve 5g. of potassium hydroxide and 2 g. of uric acid in 100 ml. of water.

**Procedure.** Dissolve the material to be tested in water or dilute hydrochloric acid, and add a solution of potassium hydroxide until the precipitated zinc hydroxide redissolves. Then add uric acid solution to form a gelatinous precipitate of zinc urate. A greenish-blue color is obtained when this precipitate is mixed with potassium persulfate and treated with the vapors of chlorine or bromine.

No similar reaction is given except with cobalt, and this reaction is easily distinguished from that caused by zinc.

To detect traces of zinc, proceed as follows:

**Procedure.** Precipitate zinc as zinc sulfide and filter the precipitate through paper. Wash and hold the paper in the vapors of hydrogen chloride, and then remove the excess hydrogen chloride with the aid of gentle heat. Treat the residue with a drop of the reagent solution and then with a 5 per cent solution of potassium ferrocyanide. A flocculent greenish-blue precipitate is formed if zinc is present.

**Detection of thallium.** Martini<sup>4</sup> has used uric acid for the microdetection of thallium.

**Procedure.** Evaporate a drop of the solution to be tested to dryness on a glass slide. Add a drop of paraffin oil and then add a concentrated solution of uric acid in 5 per cent potassium hydroxide. Tiny, colorless, lenticular crystals are formed with as little as 0.2γ of thallium.

**Detection of tungsten.** Frabot<sup>5</sup> has reported that tungsten may be detected by means of the blue color which is obtained when uric acid and sodium hydroxide are added to a tungstate. The ignited residue which is obtained after the removal of other elements reacts with uric acid and 1-2 drops of sodium hydroxide to give this blue color.

**Detection of hydrogen cyanide.** When uric acid is oxidized with nitric acid, the alloxan thus produced is transformed to an oxaluramide by means of

the hydrogen cyanide-catalyzed reaction of Deniges.<sup>6,7</sup> The details of this test are described in the section on alloxan.

1. D. Ganassini, *Soc. med. chir. Pavia Sedut.* (Jan. 29, 1909).
2. D. Ganassini, *Biochem. Centr.* 9, 482; *C.A.* 4, 2246 (1910).
3. G. Sensi and R. Testori, *Ann. chim. appl.* 19, 383-91 (1929).
4. A. Martini, *Pub. inst. investigaciones microquim., Univ. nacl. litoral (Rosario, Argentina)*. 4, 63-8 (1940); *C.A.* 36, 1264 (1942).
5. C. Frabot, *Ann. chim. anal. appl.* 2, 371-2 (1904).
6. A. Martini, *Pub. inst. investigaciones microquim., univ. nacl. litoral (Rosario, Argentina)*. 1, 61-4 (1937); *C.A.* 34, 344-5 (1940).
7. G. Deniges, *Mikrochemie.* 4, 149-54 (1926); *C.A.* 21, 2628 (1927).





# Part II

## THE OXIMES

Many oximes have been found to possess valuable analytical properties. These compounds form salts either by replacement of the hydrogen atom of the oxime group, or by the coordinating properties of the oxime nitrogen atom. Many of these salts are insoluble, and usually colored, which makes them important in analytical procedures. Most of the analytically important oximes belong to the following classes: the ortho-dioximes, the acyloinoximes, the ortho-hydroxy aromatic oximes and the monoximes of diketones. In addition, cupferron and neo-cupferron are here classed as oximes, because the nitroso-substituted hydroxyl-amines exist in tautomeric equilibria with the corresponding enol forms.

1. A. Berger, *Va. J. Sci.* 1, 151-62 (1940).

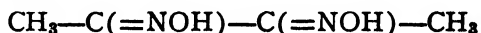


## CHAPTER VI

### THE DIOXIMES

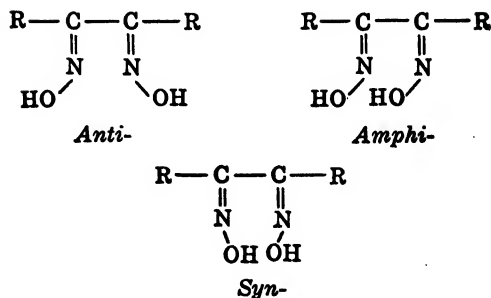
In 1905 the Russian chemist Tschugaeff<sup>1</sup> first discovered the reaction between nickel salts and the organic compound, dimethylglyoxime, which yields the brilliant-red, insoluble nickel compound,  $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$ . The insolubility of this compound has made possible the use of dimethylglyoxime as an analytical reagent for the determination of nickel. Since the discovery of this substance, various other dioximes have been investigated and used as analytical reagents.

Dimethylglyomine is the dioxime of ortho-diketone, and has the following structural composition:



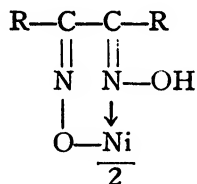
The central group,  $-\text{C}(=\text{NOH})-\text{C}(=\text{NOH})-$ , of the dimethylglyoxime molecule apparently is responsible for the formation of the nickel compound, since the replacement of the methyl groups by other aliphatic, aromatic, or heterocyclic groups does not prevent the formation of similar nickel compounds, nor does it appreciably alter the color of nickel derivatives from the characteristic scarlet-red nickel dimethylglyoxime. The dioximes also yield yellow precipitates with palladium salts, but not with the salts of any other metals. Further, it is possible to separate palladium and nickel by proper regulation of the acidity of the solution from which the precipitation is carried out. The ortho-dioxime group may therefore be considered as a specific group for nickel and palladium. The nickel compound of dimethylglyoxime corresponds in composition to the formula,  $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$ . This indicates that 1 of the hydrogen atoms of each of 2 molecules of dimethylglyoxime,  $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$ , has been replaced by the bivalent nickel atom. The resulting compound is a non-electrolyte and is non-polar in character. It is insoluble in water, but dissolves in chloroform and many other organic solvents. It sublimes without decomposition at about  $250^\circ \text{C}$ ., and obviously the scarlet color of the compound is not similar to that of most of the common salts of nickel.

From the anomalous character of the nickel derivatives we may infer that the compound is not salt-like in character, but rather owes its formation to the establishment of coordination bonds in which a ring structure is formed. The symmetric compounds, or those in which identical groups are attached to the central part of the molecule, should exist in 3 isomeric forms, according to the concept of geometric isomerism first proposed by Hantzsch and Werner. In those compounds in which the attached groups are aromatic, all 3 of the predicted isomeric forms are known. These are:



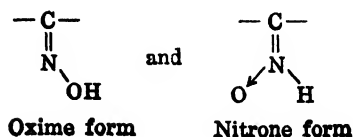
These three forms have been designated as the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -dioximes. Of these the  $\alpha$ -compound alone forms the characteristic red insoluble nickel compound. The  $\beta$ -form is totally incapable of reacting with metallic salts, while the  $\gamma$ -form gives a yellow or greenish-yellow compound with nickel, in which 1 molecule of the dioxime is attached to one atom of nickel, and the hydrogen atoms of both oxime groups are replaced by the metal.<sup>2-9</sup>

Originally the assignment of a definite configuration to each of the isomeric forms of the ortho-dioximes was made on the basis of the Beckmann Rearrangement, assuming that the groups which interchanged in the arrangement were neighboring, or *cis* groups. From this reasoning, the  $\alpha$ -form was assigned the *syn*-configuration and the nickel derivative was regarded as a 6-membered ring of the following composition: <sup>10</sup>

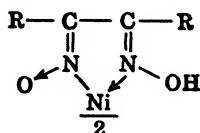


The arrow indicating a secondary valence bond, and the designation,  $\frac{\text{Ni}}{2}$  indicates that 2 such rings are attached to the nickel atom. Meisenheimer,<sup>11,12</sup> however, showed that actually the *trans* groups are interchanged in the Beckmann Rearrangement, and this has been confirmed by results obtained by the study of adsorption spectra. Following this work it was necessary to reassign new configurations to the various oximes. On this basis, the  $\alpha$ -form is regarded as having the *anti*-configuration; the  $\beta$ -form, the *syn*-configuration; and the  $\gamma$ -form, the *amphi*-configuration.

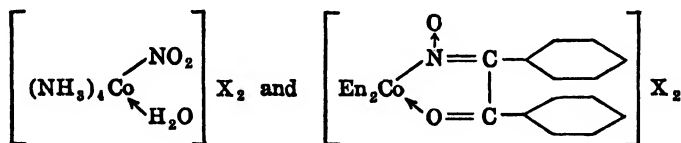
It was at first difficult to understand how a 6-membered ring could be formed from an *anti*-dioxime in which the hydroxyl groups are directed away from one another. This can be understood, however, with a knowledge of the fact that the oxime group exists in two tautomeric forms.



Brady and Mehta<sup>18</sup> have definitely proved the existence of these forms by isolating the oxygen and the nitrogen ethers corresponding to each of these structures. Actually the existence of the nitrone form of the oxime group has made possible an understanding of the formation of the nickel complexes of the ortho-dioximes. By assuming the tautomeric nitrone group to be involved in the formation of the nickel derivative, a 5-membered ring is formed in which the nickel atom is attached directly to the nitrogen atom.

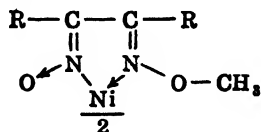


Pfeiffer,<sup>14,15</sup> who first suggested this formula, offered as evidence for this structure the fact that the metal-nitrogen linkage is quite common among coordination compounds, such as the nitro cobalt amines,  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{X}_2$  and  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{X}$ . Unlike the nitrito compounds,  $[(\text{NH}_3)_5\text{Co—ONO}]\text{X}$ , which are pink in color and unstable, the nitro cobalt amines are yellow. Pfeiffer<sup>16</sup> also found that the colors of the very similar compounds

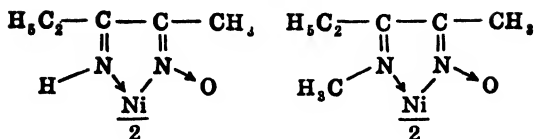


are practically identical.

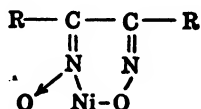
The hydroxyl radical of the second oxime group is not involved in the formation of the metal complex, and the metal is not linked to the oxygen atom. This is demonstrated by the fact that the mono-O-ether of benzildioxime forms an exactly similar compound with nickel<sup>15,17</sup>



Pfeiffer<sup>15</sup> has also shown that when 1 of the oxime groups is replaced by an imino or methylimino group, the resulting compounds form complexes in the same manner as with the ortho-dioximes



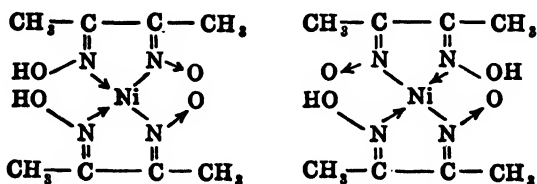
The *amphi*-dioximes ( $\gamma$ -form) form yellow or greenish-yellow compounds with nickel, in which only 1 molecule of the dioxime is attached to 1 atom of nickel. In these compounds the hydrogen atoms of both oxime groups are replaced by metal.<sup>4,5,7</sup> The metal appears to be attached to one group through the nitrogen atom and to the other through the oxygen atom, according to the following formula



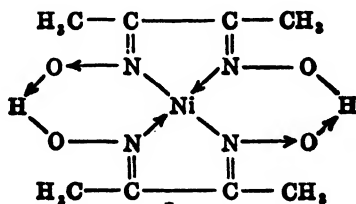
These compounds are usually not well defined and are amorphous and difficult to purify. They are stable in the presence of alkalis but in contact with acids they are rapidly converted into the red, stable, isomeric compounds of the  $\alpha$ -dioximes.

The *syn*-dioximes ( $\beta$ -form) are incapable of forming metallic complexes. According to the above discussion, it is clear that the nitrogen atom must be free on the side toward which the metal is to add and this is substantiated by the fact that neither of the mono-N-ethers of  $\alpha$ - or  $\beta$ -benzildioxime yield compounds with nickel.<sup>17</sup>

If the organic molecules in a nickel dioxime are distributed about the nickel atom in a plane, *cis-trans* isomerism may result, depending upon which of the oxime groups are joined to the nickel atom by principle and which by secondary valence bonds.<sup>18</sup>



Since no such isomerism has ever been observed, it may be concluded that there is a tautomeric shift of the hydrogen atom,<sup>19</sup> or that a hydrogen bonding may occur between neighboring oxygen atoms. Considering the latter explanation to be the more likely, Brady<sup>17</sup> assigns to nickel dimethylglyoxime the following formula:



Support is given this formulation since it explains the lack of reactivity of the hydroxyl groups of these compounds. Tschugaeff<sup>8</sup> reports that nickel dimethylglyoxime will not react with phenylisocyanate, and Barker<sup>20</sup> has found that it does not react with acetic anhydride.

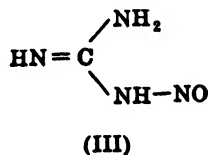
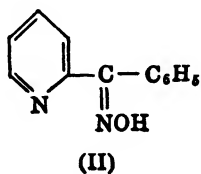
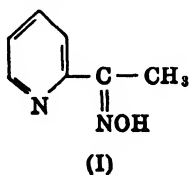
Only 1 isomer of dimethylglyoxime is known, corresponding to the *anti*-configuration. It appears that the other forms are converted into the more stable form. It is interesting to note that a temporary yellow nickel compound is first precipitated upon the addition of an acetone solution of dimethylglyoxime to a dilute and very weakly acid solution of a nickel salt, but the yellow compound rapidly changes into the red form.

The salt-forming ability of the group,  $\text{—C(=NOH)—C(=NOH)—}$ , and its specific action toward nickel salts, is definitely related to structure of the molecule of which it is a part. The dioximes of 1,2-benzoquinone and 1,2-naphthoquinone, for example, do not yield the characteristic scarlet precipitate with nickel salts. On the contrary, 1,2-naphthoquinonedioxime yields yellowish-brown precipitates with most metals, and functions, in the formation of these compounds, as a dibasic acid. Apparently, then, the aromatic ring destroys the nickel-specific action of the dioxime group. Confirmation is found in this view from the fact that 1,2-cyclohexandionedioxime (page 228), in which there are no double bonds in the ring, forms a nickel salt which is identical in appearance to that formed with dimethylglyoxime.

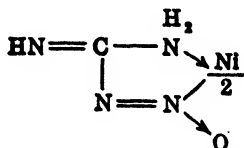
It has further been established that the group



is only one of the possible arrangements capable of conferring the property of nickel specificity upon an organic molecule. 2-Pyridyl methyl ketoxime (I),<sup>2</sup> 2-pyridyl phenyl ketoxime (II),<sup>21</sup> and nitrosoguanidine (III)<sup>22</sup> form characteristic inner-complex nickel salts.



The nitrosoguanidine complex is similar in color and solubility to that with dimethylglyoxime. It appears, then, from these studies that the fundamental requirement of a nickel-binding group is a structure whereby the nickel atom is linked to 2 nitrogen atoms by 1 principal and 1 secondary valence bond, whereby a 5-membered ring is formed.





The above discussion is taken largely from an excellent review of the applications of the dioximes to analytical chemistry by Diehl.<sup>23</sup>

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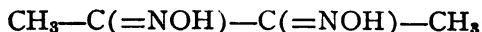
## DIMETHYLGLYOXIME

Synonym: Biacetyldioxime

$C_4H_8O_2N_2$

Beil. Ref. I, 772.

Mol. Wt. 116.12



**Use:** Detection of bismuth, cerium, cobalt, copper, insoluble silver salts, iron, nickel, oxidizing agents, palladium, platinum, reducing agents, rhenium, rhodium, tin, vanadium and basicity in slightly soluble substances.

Determination of cobalt, copper, gold, iron, lead, nickel, palladium and platinum.

Dimethylglyoxime is a white crystalline solid. It melts at 238-240° C. with decomposition. The reagent grade should be free from objectionable colored impurities, and should sublime on gentle heating without leaving a residue.

**Solubility of dimethylglyoxime.** The solubility of dimethylglyoxime in various solvents is a matter of considerable importance, since its low solubility in water is one of its most objectionable characteristics from the analytical point of view. Only 0.40 g. of the reagent dissolves in 1 liter of water, and since 3.957 g. of the reagent is required for the precipitation of 1.000 g. of nickel, the volume of the dimethylglyoxime solution required for the precipitation is unusu-

ally large. The maximum amount of nickel usually taken for an analysis is 30 mg., and thus requires 0.1197 g. of the oxime for precipitation. This is the amount contained in about 250 ml. of an aqueous solution. Obviously this is too large a volume of precipitating solution for most purposes. Because of this, a 1 per cent alcoholic solution is the commonly used reagent, and even in alcohol dimethylglyoxime dissolves with considerable difficulty. Consequently acetone has recently been substituted as a solvent for this compound. Only about 4 ml. of a 1 per cent solution of dimethylglyoxime in alcohol is required to precipitate 10 mg. of nickel. In order to carry out a successful precipitation, an excess of the reagent must be added; but when alcohol is used as the solvent, a large excess of the solution must be avoided because of the solubility of the nickel precipitate in alcohol-water mixtures, and also because of the danger of precipitating the reagent itself upon dilution of the alcohol. When 10 ml. of a 1 per cent solution of dimethylglyoxime in alcohol is added to 100 ml. of water at room temperature, and the mixture is allowed to stand, dimethylglyoxime does not precipitate; but a definite precipitate of the reagent appears within one hour when an additional 5 ml. of the reagent is added. Practically, the excess of the reagent should be even less than that indicated above, since precipitation is usually made from a hot solution from which the alcohol rapidly evaporates, and this results in a decreasing solubility of dimethylglyoxime in the mixture.

The low results in the analysis of samples containing more than 20 per cent nickel are due, according to Nussbaumer<sup>1</sup> to the solubility of the nickel precipitate in dilute ethyl alcohol. The effect of acetone on the solubility of the nickel salt has not been extensively studied.

In order to eliminate some of the difficulties encountered in the use of alcoholic or aqueous solutions of dimethylglyoxime, various workers have added the solid reagent to aqueous solutions of the nickel salt. Aqueous alkaline solutions of dimethylglyoxime have also been used as a precipitant for nickel. Such solutions do not keep well and therefore are seldom used. One such reagent, suggested by Casey,<sup>2</sup> is prepared by dissolving 1 g. of dimethylglyoxime in a mixture of 2 parts of ammonium hydroxide and 1 part of water, or by adding 3.5 g. of sodium hydroxide to 1 liter of water containing 10 g. of dimethylglyoxime.

**Synthesis of dimethylglyoxime.** Several methods have been proposed for the synthesis of dimethylglyoxime,<sup>3-6</sup> but only one is suitable for the rapid and economical preparation of large quantities of the reagent. This involves the conversion of methylethyl ketone to biacetylmonoxime by means of an alkali nitrite, followed by the oximation of biacetylmonoxime to dimethylglyoxime. Semon and Damerell<sup>3</sup> and Slotta and Jacobi<sup>4</sup> have recently studied the preparation of dimethylglyoxime and have described methods which differ only in detail.

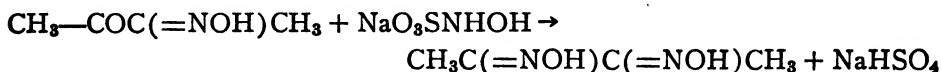
In both these procedures, biacetylmonoxime is formed by the action of gaseous ethyl nitrite on methylethyl ketone in the presence of hydrochloric acid.



According to Slotta and Jacobi, a better yield of the reagent is obtained by employing a methyl alcohol solution of hydrogen chloride as a condensing agent

rather than an aqueous hydrochloric acid solution, but in this case it is necessary to slow down the action by the addition of ether. Regardless of which procedure is employed, the biacetylmonoxime is not isolated, but is oximated directly after the removal of most of the solvent and the alcohol which is formed in the reaction.

The oximation of the biacetylmonoxime is best effected by using a solution of sodium hydroxylamine monosulfonate, which is prepared by the action of sulfur dioxide on sodium nitrite:



The following procedure is that described by Semon and Damerel.<sup>3</sup>

**Preparation of ethyl nitrite.** *Solution (a)*: Dissolve 620 g. of sodium nitrite and 210 g. of alcohol in sufficient water to make 2.5 liters of solution.

*Solution (b)*: Mix 255 ml. of concentrated sulfuric acid with 210 g. of alcohol and then add sufficient water to make 2.5 liters of solution. The ethyl nitrite used in the preparation of biacetylmonoxime may be generated continuously in the gaseous form by allowing solution (b) to flow into solution (a). A suitable mechanical arrangement must be provided to allow the mixing of these solutions at the proper rate.

**Preparation of biacetylmonoxime.** Dry 750 ml. of commercial methyl ethyl ketone over 75 g. of anhydrous copper sulfate and filter into a 2-liter, 3-necked flask, which is fitted with a condenser, a thermometer, and an inlet tube for ethyl nitrite, and so arranged that it may be cooled externally. Add 40 ml. of hydrochloric acid ( $d = 1.19$ ) and warm the mixture to 40° C. This assembly should be set up in a hood to avoid the fumes of ethyl nitrite. Now allow the ethyl nitrite, formed by mixing the above solutions, to bubble into the methyl ethyl ketone-hydrochloric acid mixture, while the latter is maintained at a temperature of 40-55° C. When all ethyl nitrite has been passed into the mixture, which requires about 1-1.5 hours, heat the mixture to distill off the alcohol formed in the reaction, and continue the heating until the temperature reaches 90° C. The crude product contained in the flask is then used immediately for the preparation of dimethylglyoxime.

**Preparation of sodium hydroxylamine monosulfonate.** Place 5,000 g. of shaved ice and 569 g. of sodium nitrite in a 12-liter jar, or similar vessel, and then add with stirring a suspension of about 1,775 g. of technical sodium bisulfite in 750 ml. of water. After the bisulfite has been added, introduce beneath the surface of the resulting solution, and with constant stirring, 150 ml. of glacial acetic acid, and then add a mixture of 550 ml. of concentrated hydrochloric acid ( $d = 1.19$ ) and 400 g. of shaved ice. Throughout all the steps in the preparation of the above mixture, the temperature should remain below 0° C. If necessary, add more ice. This solution contains sodium hydroxylamine disulfonate, and in the acid solution this rapidly hydrolyzes to the monosulfonate.

**Preparation of dimethylglyoxime.** The crude biacetylmonoxime obtained above is added immediately after its preparation to the filtered solution of sodium hydroxylamine monosulfonate. The resulting mixture is heated to 70° C. and is allowed to stand at this temperature for several hours with occasional stirring. Cool and filter, and wash the white crystalline solid with cold water until free of sulfates. The melting point of the pure compound is 238-240° C.

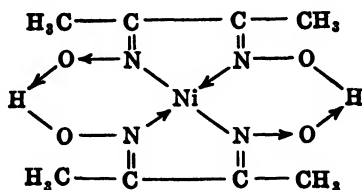
**Specifications as an analytical reagent.** To be suitable as a reagent in careful analytical work, dimethylglyoxime must meet the following requirements:<sup>276</sup>

(a) *Insoluble in alcohol:* Gently boil 2 g. of the reagent with 100 ml. of ethyl alcohol under reflux until no more of the solid dissolves. Filter on a tared filter crucible, wash with 50 ml. of alcohol, and dry at 105-110° C. The weight of the insoluble residue should not exceed 0.0010 g.

(b) *Residue on ignition*: Ignite 1 g. of the reagent at a temperature just high enough to burn off the carbonaceous matter. Cool, add 1 drop of sulfuric acid, and ignite at a dull red heat for 5 minutes. The weight of the residue should not exceed 0.0005 g.

(c) *Suitability for nickel determination:* Dissolve 1.00 g. of nickel ammonium sulfate hexahydrate in exactly 50 ml. of water. Dilute 20 ml. of this solution to 100 ml., heat to boiling, and add a solution of 0.25 g. of dimethylglyoxime in 25 ml. of alcohol. Add 1:4 ammonium hydroxide dropwise until the mixture is alkaline, and then cool and filter. To the filtrate, add 1 ml. of the nickel ammonium sulfate solution and heat to boiling. A substantial precipitate of nickel dimethylglyoxime should be formed.

**The detection of nickel.** Dimethylglyoxime, like many other of the orthodioximes of the general formula  $R-C(=NOH)-C(=NOH)-R$ , gives bright red, insoluble salts with nickel in neutral, acetic acid, or ammoniacal solutions (page 157).



Dimethylglyoxime is one of the first and one of the most useful of the orthodioximes used for the detection and determination of inorganic substances, and consequently has been very widely studied by many investigators. Apparently Tschugaëff<sup>7,8</sup> was the first to use dimethylglyoxime as a test for nickel. This test consisted of the formation of the red insoluble nickel derivative by adding dimethylglyoxime to a neutral solution of the nickel salt to be tested. The test was carried out by neutralizing the solution to be tested with ammonia, and then adding a little of the solid reagent and warming the mixture. The scarlet-red precipitate produced by even very small quantities of nickel could easily be seen against the white background of the excess insoluble reagent.

Many variations of the nickel test have been suggested, but the one given below may be considered as typical for this reaction.

**Procedure.** Heat to boiling a few ml. of the slightly acid solution to be tested and add a few drops of a 1 per cent solution of dimethylglyoxime in alcohol or acetone, and then add a dilute solution of ammonia until the mixture is alkaline. If nickel is present a scarlet-red precipitate of the inner-complex forms immediately, or on cooling, depending upon the quantity of nickel present. A red color forms with nickel concentrations as low as 1 part of nickel in 1,000,000 parts of solution. In the presence of iron or of other metals which are precipitated by ammonia, add sufficient tartaric acid to form complexes with these metals and thereby prevent their precipitation on addition of ammonia; then add the reagent.

Frequently solutions containing colored ions cannot be observed for the formation of the red precipitate, but after treating as described above, the red nickel compound may be observed by filtering the mixture, washing well, and then examining the filter paper for the insoluble compound.

Ferrous iron reacts with dimethylglyoxime and ammonia to give a ruby-red color, but this compound is soluble and need not be confused with that due to nickel, since the compound formed with the latter metal is insoluble in water. The color caused by iron fades on standing due to atmospheric oxidation of the ferrous to ferric iron unless a reducing substance is present; hence, a preliminary oxidation of the iron to the ferric state will avoid any confusion of the iron and nickel coloration. In the presence of oxidizing agents, however, nickel and dimethylglyoxime give an orange-red coloration. According to Kraus,<sup>10</sup> who first studied the reaction of nickel and dimethylglyoxime, the reaction with ferrous iron is not only confusing, due to the similarity of the colors of the nickel and ferrous compounds, but ferrous iron also renders the nickel test less sensitive.

In testing for nickel in the presence of iron, care must be taken that both ferric iron and cobalt salts are not present together in the same solution, for although neither of these metals alone is precipitated from ammoniacal tartrate solutions, when both are present together in the same solution a reddish-brown precipitate is formed which might possibly be confused with the nickel test. Weeldenburg<sup>9</sup> states that this is a complex compound of iron, cobalt and dimethylglyoxime.

Bismuth yields a yellow precipitate with dimethylglyoxime unless tartaric acid is present, and platinum and palladium yield insoluble yellow compounds having the same structure as that of the nickel salt.

Matsui and Nakazawa<sup>11</sup> claim that the dimethylglyoxime test for nickel can be applied to a mixture of metallic hydroxides by simply adding a little of the reagent to the solid hydroxides, and Matsui<sup>12</sup> claims that both nickel hydroxide and nickel sulfide react with dimethylglyoxime to form the nickel salt.

Vanossi<sup>13</sup> and Korenman and Dudnik<sup>14</sup> have used immiscible liquids to increase the sensitivity of the nickel test and to eliminate interference by other ions. Vanossi tests for nickel with the reagent and chloroform, claiming that the chloroform is effective in eliminating in the aqueous layer colored ions or

ions which interfere with the nickel test, such as nitrate, sulfite, thiosulfate, iodate, nitrite and others. Korenman and Dudnik perform the nickel test as follows:

**Procedure.** Mix 10-20 ml. of the solution to be tested with an equal amount of 1 per cent dimethylglyoxime in ethyl alcohol, and then add 0.5-1 ml. of an immiscible liquid such as benzene or carbon tetrachloride and shake. If nickel is present, a red precipitate forms at the boundary between the two liquids.

By thus concentrating the region in which the nickel precipitate is found, the sensitivity of the reaction is increased. The sensitivity and the limitations of the dimethylglyoxime reaction for nickel have been studied by Kraut,<sup>15</sup> Righellato,<sup>18</sup> Gouveia,<sup>17</sup> and Fritz.<sup>18</sup>

The test for nickel may be carried out by means of a spot technique described by Heller and Krumholz.<sup>19</sup>

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper, and treat with a drop of 1 per cent alcoholic dimethylglyoxime and hold over a bottle of ammonia. A red spot appears on the paper with as little as 0.16 $\gamma$  of nickel. This procedure may be modified by mixing a drop of the solution to be tested and a drop of a 1 per cent alcoholic solution of dimethylglyoxime in the depression of a spot plate, and then adding a small drop of dilute ammonium hydroxide. A red color or precipitate indicates the presence of nickel. The sensitivity is about the same of that using the filter paper method. The concentration limit of both reactions is about 1:300,000.

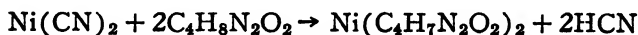
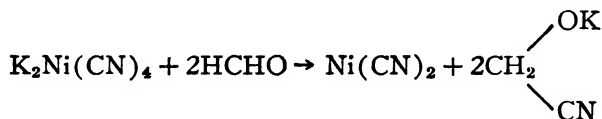
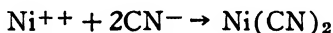
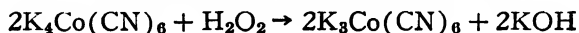
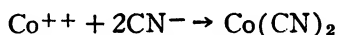
The above test may be made considerably more sensitive by placing a drop of solution to be tested on filter paper impregnated with the reagent and then allowing to dry. The reagent is prepared by soaking filter paper in a warm saturated acetone solution of the reagent and then allowing to dry. With this modification, 0.015 $\gamma$  of nickel can be detected. The concentration limit is 1:3,330,000.<sup>20</sup> By using a special spot technique, Clarke and Hermance<sup>253</sup> claim to be able to detect as little as 0.005 $\gamma$  of nickel.

**Detection of nickel in the presence of cobalt, iron, copper and manganese.** Due to the similarity in the chemical properties of nickel and cobalt, these two metals frequently occur in the same mixture, either among natural products, or in groups obtained in analytical procedures. Consequently the detection of nickel in the presence of cobalt becomes a very important procedure. Cobalt reacts with dimethylglyoxime to form dark-colored soluble compounds, and these may obscure the red color of the nickel compound, particularly if only small quantities of nickel are present in company with relatively large quantities of cobalt. Nickel can be detected in the presence of cobalt by treating the ammoniacal solution of the mixture with dimethylglyoxime, but in this case it is necessary to add a sufficient quantity of the reagent to convert all the cobalt ion present to the complex compound, and then to filter off the dark solution of the cobalt compound in order that the color of the nickel precipitate may be observed.<sup>21,22</sup>

A more satisfactory procedure, however, has been devised by Middleton and Miller.<sup>23</sup> Cobalt is converted into the cobalticyanide ion by treatment with sodium cyanide and exposure to air; and then, after the addition of dimethylglyoxime, the complex nickel cyanide, which is also formed when sodium cyanide is added to the solution containing both ions, is decomposed by the dropwise addition of a solution of silver nitrate. Silver nitrate decomposes the nickel complex to form the free nickel ion, which reacts with the dimethylglyoxime to give the characteristic red precipitate, but the cobalticyanide ion is not affected by this treatment. The following procedure may be used.

**Procedure.** Add a solution of sodium or potassium cyanide to the solution to be tested until the precipitate which first forms just dissolves, and then heat for 5 minutes and dilute with hot water to 50 ml. Add a little 1 per cent alcoholic dimethylglyoxime, and then a solution of silver nitrate dropwise until a pink precipitate appears. In this way 0.0002 mg. of nickel per ml. can be detected. As little as 0.02 mg. of nickel in the presence of 2,600 times as much cobalt gives a pink precipitate within 30 minutes.

More recently Feigl and Kapulitzas<sup>24</sup> have proposed a modification of the cyanide method in which the nickel cyanide complex is decomposed by the addition of formaldehyde with the liberation of the nickel ion, while the more stable cobalticyanide is unaffected. The procedure consists in converting both nickel and cobalt ions to the complex cyanide,  $K_2[Ni(CN)_4]$  and  $K_3[Co(CN)_6]$ , by the addition of potassium cyanide and hydrogen peroxide, then destroying the nickel complex by the addition of formaldehyde, and finally testing for nickel by the usual procedure employing dimethylglyoxime. Since the cobalt complex is not affected by formaldehyde, cobalt remains inactive toward dimethylglyoxime. The chemical changes occurring during these reactions are as follows:<sup>25-28</sup>



Iron, if present, is converted to ferricyanide, which like the cobalt complex is not decomposed by formaldehyde; consequently the test for nickel may also be made in the presence of iron, or of iron and cobalt together. The following

procedure may be used for the detection of small amounts of nickel in cobalt salts.<sup>24,29</sup>

**Procedure.** Dissolve 0.5-1.0 g. of the cobalt salt to be tested in 2-3 ml. of water, and to this solution add drop by drop a concentrated solution of potassium cyanide until the precipitate which first forms just dissolves. Warm the solution and add hydrogen peroxide until the mixture is honey-yellow in color. This indicates that the cobaltous compound has been oxidized to the cobaltic compound. Then evaporate the solution until it becomes viscous, and add an excess of solid dimethylglyoxime. Heat the solution to 50-60° C., and then add dropwise a 40 per cent solution of formaldehyde until the odor of the latter is perceptible. The red nickel derivative of dimethylglyoxime separates immediately, or upon cooling, if nickel was present in the unknown. If the mixture is shaken with 1-2 ml. of ether, the precipitate is concentrated as a red film in the zone between the water and the ether layers, thus rendering the test somewhat more sensitive.

The same procedure may be used for detecting small amounts of nickel in the presence of large amounts of cobalt and iron. The method of Feigl<sup>24,259</sup> may also be applied as a drop reaction.

**Procedure.** Place 0.05-0.06 g. of the water-soluble cobalt salt, which is to be tested for nickel, on a spot plate; and in an adjacent depression place a similar quantity of a cobalt salt which is known to be nickel-free. Dissolve each sample in 1-2 drops of water, and then add dropwise and with stirring a saturated aqueous solution of potassium cyanide until the precipitate which is first formed is dissolved. Then add 1-2 drops of 3 per cent hydrogen peroxide and stir until the solution is bright yellow in color. This may require a few minutes. Next add to each sample a few milligrams of dimethylglyoxime and a few drops of 40 per cent formaldehyde and again stir. If nickel is present, a red precipitate forms or an orange-red color appears. The sample containing no nickel remains yellow, and a comparison with the test drop makes possible the detection of very small quantities of nickel.

A drop reaction or spot test which may be used to detect nickel in the presence of cobalt, copper and manganese has been proposed by Heller and Krumholz.<sup>19</sup> The drop reaction may be carried out as follows:

**Procedure.** Mix 1 drop of the acid solution to be tested with 1 drop of 3 per cent hydrogen peroxide and 1 drop of a saturated solution of sodium carbonate on a spot plate. If large quantities of cobalt are present, a green precipitate forms, and this slowly darkens to form cobaltic oxide. If small quantities of cobalt are present a green coloration appears. Now add 1 drop of a 1 per cent alcoholic solution of dimethylglyoxime, and if nickel is present the characteristic red color of the nickel compound is formed on the upper surface of the liquid. By this method 1.25γ of nickel may be detected in the presence of 200 times as much cobalt. The concentration limit is 1:40,000.

The same procedure may be employed when both cobalt and manganese are present, but due to the formation of dark manganese dioxide the sensitivity of the



reaction is somewhat reduced. As little as 2.5 $\gamma$  of nickel, however, may be detected in the presence of 80 times as much cobalt and manganese.

Small quantities of nickel may be detected in the presence of large quantities of cobalt and copper or manganese by means of a spot test described by Feigl.<sup>80</sup>

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper that has been impregnated with dimethylglyoxime, and then immerse the paper in a dilute ammonium hydroxide solution. By gently agitating the paper in the solution, the colored compounds, which both cobalt and copper form with dimethylglyoxime, are dissolved, and the red spot due to the nickel compound remains on the paper. By this procedure 0.8 $\gamma$  of nickel at a concentration limit of 1:62,500 may be detected in the presence of 1,250 times as much cobalt, and 1.7 $\gamma$  of nickel at a concentration of 1:29,400 may be detected in the presence of 590 times as much copper.

This method cannot be used in the presence of manganese due to the formation of manganese dioxide. If, however, the paper which has been spotted with the solution to be tested is immersed in an ammonium carbonate solution, manganese dioxide is not formed; but unfortunately the copper and the cobalt dimethylglyoxime compounds are not completely dissolved. Consequently, the use of ammonium carbonate can be recommended only for detecting nickel in the presence of manganese. As little as 0.1 $\gamma$  of nickel at a concentration limit of 1:500,000 can be detected by this method in the presence of 10,000 times as much manganese.

Tananaev<sup>31,248</sup> has attempted to use dimethylglyoxime for the detection of nickel in the presence of other ions, and has found that the presence of large quantities of copper masks the test for nickel, but that this interference may be eliminated if a large quantity of potassium thiocyanate is present. Tananaev performs the test by adding a drop of the solution to be tested to filter paper which has been impregnated with potassium thiocyanate, then exposing to ammonia gas, and finally adding a drop of the dimethylglyoxime reagent. A better test is obtained if the filter paper is impregnated with diammonium hydrogen phosphate solution, dried, and treated with a little of the solution to be tested, then with dimethylglyoxime, and finally exposed to ammonia vapor.

The dimethylglyoxime reaction has been widely used for the differentiation of nickel and cobalt by the simple process of adding the reagent to a solution containing the two ions, but Cerdan and Ferrer<sup>32</sup> claim that the reactions with xanthogenates are more suitable. A comparison of potassium methyl xanthogenate with dimethylglyoxime for the detection of nickel alone shows that both reagents are about equally sensitive and are capable of detecting nickel in concentrations as low as 1:100,000. For detecting nickel when present with 10 times as much cobalt, the xanthogenates are not very satisfactory for nickel concentrations below 1:40,000, while dimethylglyoxime is most sensitive between 1:1,000 and 1:50,000. In the presence of 50 times as much cobalt, nickel can be detected with xanthogenates at a concentration of 1:25,000; and in the presence of 100 parts of cobalt, at a concentration of 1:20,000. Dimethylglyoxime is sensitive in the last case only for nickel concentrations above 1:10,000. It

is possible to detect nickel by means of xanthogenates in the presence of 200 times as much cobalt.

Nickel can be detected by means of dimethylglyoxime in the presence of considerable quantities of ferric salts by means of a drop reaction performed as follows:<sup>19</sup>

**Procedure.** Place a drop of the solution to be tested on a spot plate, and to this add a drop of saturated sodium tartrate solution, 2 drops of saturated sodium carbonate solution, and finally a drop of a 1 per cent alcoholic solution of dimethylglyoxime. In the presence of nickel a red precipitate forms at the surface of the liquid. As little as 0.5 $\gamma$  of nickel, at a concentration limit of 1:100,000, can be detected in the presence of 1,000 times as much iron in a 2 N hydrochloric acid solution.

**Detection of nickel in steel and alloys.** Nickel may be detected in steel and various alloys by suitable applications of the dimethylglyoxime test, which has been described in the preceding sections. Typical of these is a method described by Danheiser<sup>38</sup> for the rapid detection of nickel in steel.

**Reagent.** Mix 10 ml. of a 1 per cent alcoholic solution of dimethylglyoxime with a solution of 5 g. of nitric acid in 90 ml. of ammonium hydroxide ( $d = 0.90$ ).

**Procedure.** Place a few small shavings of the steel to be analyzed on a watch glass and warm with a drop of concentrated nitric acid, and then add a drop of the reagent. If nickel is present, the mixture becomes rose-red in color, and under the microscope pink crystalline needles may be observed.

Van Heteren and Van der Warder<sup>39</sup> have used the method of Tschugaev for the detection of nickel in the alloy used for coinage metal.

It is often necessary to test steel and various alloys for the presence of nickel without destroying the object to be tested. This may easily be accomplished by any of a variety of tests which may be applied to the surface of the metal.<sup>40,42-47,271</sup> Typical of these is a test proposed by Williams.<sup>40</sup>

**Reagent.** An acid solution used to dissolve the nickel from the metal is prepared by mixing 25 ml. of water, 10 ml. of concentrated sulfuric acid, 10 ml. concentrated nitric acid, 10 ml. of phosphoric acid, and 10 g. of citric acid.

**Test paper.** Immerse a strip of filter paper in a solution obtained by mixing 10 g. of citric acid, 25 ml. of water and 10 ml. of a 1 per cent solution of dimethylglyoxime in isopropyl alcohol.

**Procedure.** Place 1 drop of the acid mixture on the clean surface of the steel or alloy to be tested and allow to stand for 15-30 seconds. Then take up the drop with the prepared reagent paper and treat with 2-4 drops of 30 per cent potassium hydroxide solution. A red coloration appears with steels containing from 0.5-35 per cent of nickel.

Nickel may be detected in steel or nickel-plated objects as follows:

**Procedure.** Moisten the polished surface with 1:1 hydrochloric acid, and allow the acid to react for about 30 seconds. Then take up the resulting drop with filter paper, make alkaline with 1:1 ammonium hydroxide and add an alcoholic solution of dimethylglyoxime.

Koenig<sup>44,45</sup> has used aqua regia to dissolve the metal in order to insure the complete oxidation of the iron, since ferrous iron, which is obtained by using hydrochloric acid, gives a red color with dimethylglyoxime, and might prove confusing.

Jirkovsky<sup>46</sup> has used an electrolytic corrosion method to detect small quantities of nickel in steel without injuring the specimen. The metal to be analyzed is made the anode of an electrolytic cell, and is separated from the cathode by means of a sheet of filter paper which is saturated with dimethylglyoxime. After a short time the red color of the nickel dimethylglyoxime compound on the paper shows the distribution of the nickel in the specimen analyzed.

Fortini<sup>42</sup> has suggested the following method for testing for nickel in alloys:

**Reagent.** Dissolve 0.5 g. of dimethylglyoxime in 5 ml. of 98 per cent alcohol and add 5 ml. of ammonium hydroxide.

**Procedure.** All fat and oil is removed from the surface of the metal with ether, and add a drop of the reagent. The red nickel compound is formed if nickel is present, and this may be more readily observed by rubbing a strip of filter paper over the stain. The test is made more sensitive by heating the surface to be tested in the oxidizing flame of a blow pipe before applying the test.

Nechamkin and Sanders<sup>257,269</sup> have used dimethylglyoxime for the detection of nickel in metal coatings and Edwards has used a similar test for nickel in high-conductivity alloys.

**Detection of nickel in fats.** Dimethylglyoxime may be used conveniently for the detection of small quantities of nickel in fats.<sup>48</sup>

**Procedure.** Add 10 ml. of hydrochloric acid ( $d = 1.12$ ) to 10 g. of the fat to be tested and heat for 2 or 3 hours on a steam bath with frequent shaking. Filter the mixture through a wet filter paper to remove the fat, and collect the filtrate in an evaporating dish. Evaporate the filtrate on a steam bath, and when it is partially evaporated add 2-3 ml. of concentrated nitric acid to insure the destruction of all organic matter, and then continue the evaporation to dryness. Dissolve the residue in a few ml. of water and treat with a few drops of dimethylglyoxime solution and a few drops of ammonium hydroxide. A characteristic red color of nickel dimethylglyoxime appears if nickel is present.

Wagenaar<sup>49</sup> and Ranedo<sup>50</sup> have used dimethylglyoxime for the detection of traces of nickel in hydrogenated oils. The following procedure has been proposed by Wagenaar.<sup>49</sup>

**Procedure.** Melt a portion of the fat to be analyzed in a porcelain dish which is placed on a water bath, and insert vertically a strip of ashless filter paper 20 x 2.5 cm. which has been rolled into a cylinder around a thin platinum wire. The paper takes up the melted fat and when ignited at the top serves as a wick for the combustion of the fat. By this procedure loss of nickel during

the combustion of the fat in the soot from the flame is eliminated. Add the remainder of the fat at intervals until finally it has all been consumed by combustion. Then ash the paper in a silica or platinum crucible, moisten with hydrochloric or nitric acid, evaporate to dryness, and treat with ammonium hydroxide and dimethylglyoxime in the usual manner. The formation of dichroic, rose-colored needles indicates the presence of nickel. By this procedure as little as 0.03 mg. of nickel can readily be detected in 30 g. of fat, corresponding to 1 part in 1,000,000. A positive, though less distinct test, may be obtained with 1 part of nickel in 10,000,000 parts of fat.

**Detection of nickel in silicates.** Hackl<sup>51</sup> and Harwood and Theobald<sup>52</sup> have used dimethylglyoxime for the detection of small quantities of nickel in silicate rocks. For the details of this procedure, see section on determination of nickel in rock analysis (page 187).

**Detection of nickel in the ash of biological materials.** Armit and Hardin<sup>21</sup> have used dimethylglyoxime for the detection of nickel in the ash of biological materials. The procedure is essentially the same as that described by Tschugaev.<sup>7,8</sup>

**Detection of nickel in systematic schemes of qualitative analysis.** A great many authors have used dimethylglyoxime as a test for nickel after its separation from other metals according to the usual practices in systematic analysis.<sup>53-63,249-251,254</sup> As a rule nickel is accompanied by cobalt with which it is precipitated as the sulfide. The sulfides are dissolved in aqua regia, and after the excess acids have been removed by evaporation, the test is applied by means of the well-known procedures.

Charlot and Bezier<sup>273</sup> have used dimethylglyoxime in a scheme of analysis whereby nickel is detected in the presence of various other cations without previous separation.

**Microdetection of nickel.** Kirschner<sup>83</sup> and Korenman<sup>84-86</sup> have used dimethylglyoxime as a microchemical reagent for detecting small quantities of nickel. In a dark field the nickel dimethylglyoxime precipitate appears as emerald green needles. By using the microscope it is possible to detect nickel in a solution containing 1 mg. of nickel and 500 mg. of iron in 3 liters of water.<sup>83</sup>

Nickel may be detected in alloys by identifying microscopically the red nickel dimethylglyoxime crystals which are obtained as follows:

**Procedure.** Treat a fragment of the metal, or the metal surface, with a small drop of 2 N nitric acid solution containing a little nitrous acid; and then expose the resulting solution to ammonia fumes. Add a drop of a solution prepared by diluting 5 ml. of a saturated solution of dimethylglyoxime in concentrated ammonium hydroxide with 10 ml. of 95 per cent ethyl alcohol. Iron yields a red solution but no precipitate.

As little as 0.006% of nickel can be detected in 1 ml. of solution at a dilution of 1:160,000,000 with  $(\text{NH}_4)[\text{Hg}(\text{SCN})_4]$  by means of an improved induced test with zinc ions and dimethylglyoxime.<sup>86</sup> According to Korenman,<sup>87</sup>



nickel is present, a deep red or orange-red filtrate is obtained, but in the absence of nickel the filtrate is pale yellow.

Feigl claims that this reaction is about 4 times as sensitive as the Tschugaev test.

Rollet<sup>65</sup> has used this reaction for the detection of nickel in various materials, but has substituted an aqueous solution of bromine for the lead peroxide as the oxidizing agent.

**Procedure.** Add a slight excess of an aqueous solution of bromine to the solution to be tested and add sufficient ammonium hydroxide solution to react with all the bromine. Then add a few drops of a 1 per cent alcoholic solution of dimethylglyoxime. An orange to red color develops within 2 minutes if the original solution contained 0.0005 mg. of nickel per ml. By using a greater volume of the test solution it is possible to detect as little as 0.015 mg. of nickel per liter.

This test may be applied as a drop reaction.

**Procedure.** Mix 1 drop of the solution to be tested with 1-2 drops of bromine water on a spot plate, and add a little ammonium hydroxide until the color of bromine disappears. Then add a drop of a 1 per cent alcoholic solution of dimethylglyoxime. In the presence of nickel a red or orange color appears within 1-2 minutes. As little as 0.12% of nickel at a concentration limit of 1:400,000 can be detected in this way.

Bromine water may be replaced in the above procedure by ammonium persulfate and a small amount of silver nitrate.<sup>66</sup>

Vanossi<sup>67</sup> has proposed the following method for detecting nickel in the presence of cobalt and iron:

**Procedure.** Heat a 0.5-1.0 M solution of a cobalt salt to 60-80° C., and then add drop by drop 2-3 M potassium cyanide solution until the precipitate which forms is dissolved. Avoid an excess. Heat 1-2 minutes until the dark red color of the solution changes to yellow, and then without cooling add 0.05-0.2 ml. of 1 per cent alcoholic dimethylglyoxime solution and 3-8 drops of 28 per cent formaldehyde solution. Allow to stand 5 minutes at 60-80° C., and cool. Add 0.1-0.3 ml. of chloroform, shake vigorously, and by means of a pipet transfer the chloroform layer to another tube and add 1-2 drops of water. Stir until the mixture is colorless, and add a saturated bromine solution dropwise to the appearance of a yellow color, and then concentrated ammonium hydroxide until the yellow color disappears. Finally add 1-2 drops of 1 per cent alcoholic dimethylglyoxime solution and shake well. In the presence of nickel a red color appears in the aqueous layer. This method can be used only in the presence of several per cent of iron, and can be used in solutions containing 6.1-0.15% of nickel and 10 mg. of cobalt salt.

Vanossi<sup>67</sup> has also proposed a method for detecting nickel in iron salts which contain no cobalt.

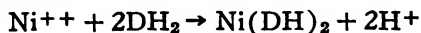
**Procedure.** To detect nickel in the presence of ferric salts which contain no cobalt, add to the ferric solution an excess of 2.5 M citric acid, make alkaline with ammonium hydroxide, add dropwise dimethylglyoxime solution, remove the chloroform layer as above and treat as previously with citric acid, bromine and dimethylglyoxime. By this method 0.08% of nickel can be detected in 0.03-0.06 ml. of a molar iron solution and 0.15-0.2% of nickel can be detected in 0.3-0.5 molar solution.

Small quantities of nickel may be detected in the presence of silver by the method of Fischer and Cayard.<sup>68</sup> According to this procedure dimethylglyoxime is added to an ammoniacal solution containing the silver and nickel complex ions and a little ammonium persulfate. As little as 0.2% of nickel can be detected in 2 mg. of metal by means of the red color which forms.

In a critical review of the various reagents which have been used for the detection of nickel, Wenger, Duckert and Busset<sup>69</sup> recommend the use of dimethylglyoxime.

**Gravimetric determination of nickel.** In a series of investigations, Brunck<sup>70-74</sup> applied the Tschugaev reaction to the separation and gravimetric determination of nickel. In these investigations Brunck studied the completeness of precipitation of nickel by dimethylglyoxime from both ammoniacal solutions and solutions buffered with acetate, and he also studied the separation of nickel from iron, aluminum, chromium, cobalt, manganese and zinc. The results proved highly satisfactory, and the procedures which he developed have since been widely used for the separation and determination of nickel. Since that time many papers have appeared,<sup>75-89</sup> all of which tend to confirm the results obtained by Brunck, and among these are to be found many additional separations. There are few serious objections to the use of dimethylglyoxime for the gravimetric determination of nickel, but in general not more than 30 to 50 mg. of the metal can be determined owing to the bulkiness of the precipitate. Many problems arise in connection with the use of dimethylglyoxime as a precipitant for nickel due to co-precipitation of iron and cobalt when both are present in the nickel solution, but generally these difficulties have been overcome by proper attention to detail in the procedure.

Two hydrogen ions are liberated when one nickel ion is precipitated according to the following equation:



(DH<sub>2</sub> = dimethylglyoxime), and thus it will be seen that precipitation is complete only from solutions containing an excess of ammonia, or from solutions buffered by acetate. Since the nickel dimethylglyoxime precipitate is soluble in strong acids, the presence of a large amount of acetic acid in the solution from which precipitation occurs exerts a noticeable solvent action upon the precipitate, and consequently satisfactory results are obtained only when the greater portion of any mineral acid present is neutralized by the addition of a strong base, and the remaining acid neutralized by the addition of sodium acetate. The presence of a moderate quantity of free ammonia has no effect

on the precipitation, and an excess of ammonium salts appears to do no harm, although the precipitate is soluble in strongly alkaline solutions with the formation of a yellow color.<sup>90</sup> The nickel precipitate is also soluble in cyanide solutions. The presence of an excess of the reagent is without effect on the precipitation, but too large an excess should not be used, since there is a distinct possibility that the dimethylglyoxime used in the determination may be precipitated due to its low solubility in water, and also because of the solvent action of alcohol-water mixtures upon the nickel precipitate.

**Determination of nickel in the absence of interfering substances.** The gravimetric determination of nickel in the absence of interfering substances offers no special problems. The precipitation is carried out in much the same manner as that used in the detection of nickel, although special precaution must be taken to insure completeness of precipitation and the formation of a pure precipitate.

The solubility of nickel dimethylglyoxime has been studied by Nuka,<sup>91</sup> who has found that less than 0.1 mg. of the precipitate dissolves in 100 ml. of cold water, while in hot water the solubility increases to 0.6 mg. of the nickel compound in 100 ml. Thus, if the precipitate is filtered from a hot solution, the loss of nickel may be appreciable, and may represent a relatively large proportion of the nickel if only small quantities of nickel were originally present. In fact, since usually not more than 30 mg. of nickel are determined, the error may be relatively large. Studies have shown that a precipitation of nickel dimethylglyoxime may occur from the filtrate obtained when the precipitate has been filtered from hot solution, although this never corresponds to more than 0.1 or 0.2 mg. of nickel.<sup>74,78</sup> A more serious source of error lies in the use of too large a volume of alcoholic solution of the reagent. Due to the increased solubility of the nickel precipitate in alcohol-water mixtures, some loss may occur when much alcohol is present. It is of interest to note that according to the investigations of Nuka, the presence of alcohol in the cold solution does not appreciably increase the solubility of the nickel precipitate, and this is additional cause for cooling the solution from which precipitation has taken place before filtering. Further, Nuka recommends that the solution cool for at least 1 hour after precipitation, and that cold water be used to transfer and wash the precipitate. The solubility of nickel dimethylglyoxime in various media is given in Table 29.

TABLE 29.

Composition of Solution (Total volume 500 ml.)	Solubility of Nickel Dimethylglyoxime per 100 ml.
Cold water .....	0.1 mg.
Hot water + 0.2 g. dimethylglyoxime .....	0.6 mg.
Hot water + 0.5 g. dimethylglyoxime .....	0.5 mg.
Hot water + 0.2 g. dimethylglyoxime + 150 ml. hot alcohol .....	1.5 mg.
Hot water + 0.2 g. dimethylglyoxime + 100 ml. hot alcohol .....	1.1 mg.
Hot water + 0.2 g. dimethylglyoxime + 50 ml. hot alcohol .....	0.8 mg.
Cold water + 0.2 g. dimethylglyoxime + 100 ml. hot alcohol .....	0.1 mg.



In order to eliminate some of the difficulties inherent in any method employing an alcoholic solution of dimethylglyoxime as the precipitant. Nuka has recommended a procedure in which solid dimethylglyoxime is used. This is added to a cold nickel solution, the solution is then heated to boiling, and precipitation is brought about by the addition of ammonia. The solution is then cooled before filtration. The presence of an excess of the solid reagent in the precipitate causes no difficulty, since it sublimates at the temperature of 120° C., which is commonly used for drying the nickel precipitate.<sup>91-94</sup>

According to Nagai<sup>95</sup> nickel dimethylglyoxime is best precipitated at a pH range of 7.5 to 8.1. The procedure which he recommends is to add first dimethylglyoxime to the nickel solution and then neutralize the free acid with 0.1 N ammonium hydroxide, using neutral red or *m*-nitrophenol as the indicator.

Unsatisfactory results have been reported with the gravimetric method when only small quantities of nickel are present. When the amount of nickel is less than 0.06 per cent, a part of the nickel is not precipitated with dimethylglyoxime even after long standing; and there seems to be some doubt as to whether the determination is accurate when the usual quantity of the sample is employed. Jones<sup>187</sup> analyzed steel known to contain as high as 0.1 per cent of nickel by the gravimetric method and found only traces of nickel present. To determine the loss of nickel under such conditions, Jones precipitated definite quantities of nickel in the usual manner from a volume of 100 ml.; and, after standing overnight, filtered the mixture through a close pulp filter, but did not wash the precipitate. He then determined nickel in the filtrate by a colorimetric method which will be described later. The results of this study are given in Table 30.

TABLE 30.

Grams of Nickel Used	Percentage of Nickel in Filtrate
0.0001	35.0
0.0002	7.5
0.0003	5.0
0.00075	2.0
0.0010	2.25
0.0015	1.0
0.0020	0.25
0.0025	Negligible

From these results it may be seen that the gravimetric method should not be employed with very small quantities of nickel. Colorimetric procedures appear to be definitely superior for quantities of nickel less than 0.0025 g.

The effect of oxidizing agents upon the completeness of precipitation of nickel dimethylglyoxime has been discussed in a preceding section (page 174), but the disturbing effect of nitrates in the precipitation of nickel has never been clearly stated. There appears to be no doubt but that nitrate does prevent the precipitation of small amounts of nickel,<sup>52</sup> and this may very well be the explanation for the low results obtained by Jones in the analysis of steels containing less than 0.06 per cent of nickel. On the other hand, nitrate is usually present in

the mixtures employed in the determination of nickel in steel, and reliable results are obtained in these procedures. If the low results obtained in the presence of nitrate are due to the formation of tetravalent nickel, and this seems the likely explanation, tartrates or citrates, which also are present during the determination to keep iron in solution, may act as reducing agents and therefore counteract the effect of the oxidizing action of the nitrates. While this is proposed as a possible explanation of the satisfactory results obtained in the determination of nickel in steel, it must be mentioned that tartrate was also present in the determinations reported by Jones, and in this case the results still were low. From this discussion it will be seen that the effect of nitrate upon the nickel determination has not yet been definitely established.

The precipitate of nickel dimethylglyoxime is anhydrous and is readily dried at 110-120° C., and it is not hygroscopic.<sup>91</sup> It may be weighed as such, and this is the most convenient and accurate method, although the precipitate may be ignited to nickel oxide, NiO, and weighed in that form, or it may be dissolved in nitric acid and the nickel titrated by means of a solution of cyanide.

The following procedure is the one commonly used for determining nickel in the absence of interfering substances. When interfering metals are present, and this is frequently the case, the procedure must be modified so as to eliminate such interference. These methods will be discussed in the later sections. The procedure described here is the one generally accepted as standard, and is essentially the same as that originally proposed by Brunck.

**Reagent.** Prepare a 1 per cent solution of dimethylglyoxime in alcohol or acetone.

**Procedure.** Make a solution containing not more than 0.050 g. of nickel slightly acid and dilute to a volume of 100-150 ml., and heat to boiling. Add 4 ml. of the reagent for each 10 mg. of nickel present, and then an additional 5 ml. in excess. Then precipitate nickel by adding ammonium hydroxide solution until the mixture is slightly alkaline. Allow the precipitate to stand for 1 hour until it is cold, and filter through a Gooch crucible. Wash well with cold water, dry for 1 hour at 120° C., and weigh. The weight of nickel present is found by multiplying the weight of precipitate by 0.2032.

It should be added that fairly reliable results may be obtained by a much more rapid procedure proposed by Dick,<sup>96</sup> in which the precipitate is filtered from the hot solution without standing, washed with hot water, alcohol and ether, and then dried by aspirating air through it for 2 or 3 minutes, and then weighed. Dick claimed excellent results, but sufficient data are not included in his work to justify the complete acceptance of his claims. From his work, however, it appears that the method may be satisfactory where high accuracy is not required.

Aleksandrov<sup>274</sup> has recently reported that in the determination of small quantities of nickel, an appreciable error is introduced if the dimethylglyoxime precipitate is filtered through fritted glass crucibles. This is said to be caused by the solubility of the glass in dilute ammonia.

Various procedures have been proposed in which the precipitate of nickel dimethylglyoxime is ignited to nickel oxide, NiO, before weighing.<sup>74,75,79,97-101</sup>

According to some authors this method yields accurate results, but according to others is not satisfactory. These conflicting claims may be due to a difference in the techniques employed; the nickel compound begins to sublime at  $250^{\circ}\text{C}$ ., and unless special precautions are taken there may be some loss from this cause. The most satisfactory results have been obtained when the precipitate is wrapped in two thicknesses of moist filter paper and the mass charred at as low a temperature as possible before burning away the filter paper. The following procedure is suggested:

**Procedure.** Precipitate nickel dimethylglyoxime as described in the above procedure, and filter on paper. Wash well with cold water, and wrap the precipitate in the moist paper and place in a weighed porcelain crucible. Char the paper by heating at as low a temperature as possible without burning. Note carefully that the finely divided precipitate is not carried away mechanically by the escaping gases. After the paper is thoroughly charred, ignite the precipitate in the presence of sufficient air. Cool, and weigh as nickel oxide,  $\text{NiO}$ , which contains 78.58 per cent nickel.

Still a third method of treating the nickel precipitate is to dissolve in nitric acid and complete the determination of nickel by means of a cyanide titration.<sup>102-107</sup> The following procedure is recommended:

**Procedure.** Precipitate nickel in the usual manner and filter the precipitate on paper and wash well with water. Dissolve the precipitate of nickel dimethylglyoxime on the paper with hot 5:1 nitric acid and wash the paper well with water. Add a few drops of hydrochloric acid to the filtrate and boil for 5 minutes to destroy the dimethylglyoxime and to expel chlorine and the oxides of nitrogen. Cool, dilute, neutralize with ammonium hydroxide, and proceed with the cyanide titration according to established procedure, using the silver iodide end-point,<sup>108,109</sup> or by a potentiometric titration using a silver or silver sulfide indicator electrode.<sup>102</sup>

**Determination of nickel in the presence of iron.** Iron is one of the metals most commonly associated with nickel in the materials which the chemist is most frequently called upon to analyze. These include both natural and metallurgical products. One of the greatest advantages possessed by the dimethylglyoxime method of determination is that by its use nickel and iron can be conveniently separated. There are, however, several considerations which must be born in mind in carrying out the analysis of nickel when in the presence of iron salts. The precipitation of the nickel compound can be made only from an ammoniacal solution, or from one buffered with acetate, and under both conditions iron is precipitated also; in the former case the insoluble hydrous oxide is formed, and in the latter, the basic acetate. Four procedures have been suggested by means of which this difficulty can be overcome. The first of these calls for the removal of iron as ferric chloride from an acid solution by an ether extraction, although this method is not generally recommended.<sup>75,79</sup> The iron may also be removed by precipitating with an excess of ammonium hydroxide, which dissolves the nickel with the formation of the nickel ammonia complex.<sup>99</sup> In a third method iron is not removed from the solution, but is pre-

vented from precipitating by the formation of a complex with added tartrate or citrate. In the fourth procedure, iron is reduced to the ferrous condition, in which form it is not precipitated from a boiling acetate solution.<sup>71,74</sup>

The formation of the ferric tartrate complex, which was suggested by Brunck,<sup>71,74</sup> is the one most extensively employed in analysis of iron and steel. According to Rothschild,<sup>110</sup> however, iron and nickel cannot be satisfactorily separated from an ammoniacal tartrate solution, although it appears from his work that cobalt may also have been present.

The following procedure may be used for the determination of nickel in iron and steel:

**Procedure.** The size of the sample varies according to the nickel content; since, because of the bulkiness of the precipitate, not more than 30 mg. of nickel must be present. The quantity of sample used with nickel steels of different nickel content is shown in Table 31.

TABLE 31.

Per Cent of Nickel	Weight of Sample Used
0 to 1 per cent nickel	3 g.
1 to 3 per cent nickel	1 g.
3 to 6 per cent nickel	0.5 g.
Above 6 per cent nickel	0.25 g.

Determine the weight of sample to be used from Table 31, and weigh into a 400 ml. beaker. Add 30 ml. of hydrochloric acid and heat until the steel is dissolved, and then add 10 ml. of nitric acid to decompose any carbides which remain, and to oxidize iron to the ferric state. Boil for 15 minutes and dilute with distilled water to 200 ml. Add 40 ml. of a 20 per cent aqueous solution of tartaric acid, and neutralize with ammonium hydroxide, and then add 1.0 ml. in excess. Filter off any insoluble material which remains, and wash the filter with hot water containing a little ammonia. Make the filtrate slightly acid with acetic acid, heat to 60° C., and add 20 ml. of a 1 per cent alcoholic or acetone solution of dimethylglyoxime. Then add ammonium hydroxide dropwise until the solution is slightly alkaline, and digest for 30 minutes at 60° C. If copper is present, more dimethylglyoxime should be added and the mixture should be allowed to stand for several hours. Let stand at least one hour and filter the cold solution through a Gooch crucible or glass filter crucible, keeping the crucible filled with the liquid. Wash the precipitate with cold water and dry at 110-120° C., and weigh as nickel dimethylglyoxime. The factor for nickel is 0.2032.

The above procedure may be modified by igniting the precipitate to nickel oxide or by dissolving in nitric acid and completing the determination by the cyanide titration as described above.

Rubricus<sup>99</sup> has described a procedure whereby interference by iron is eliminated by precipitating with ammonium hydroxide. His method is as follows:

**Procedure.** Dissolve about 2 g. of the sample of steel containing 3-5 per cent nickel in 40 ml. of hot 6 N nitric acid. Transfer the solution to a 500 ml. calibrated flask and add slowly, with shaking, 250 ml. of 6 N ammonium hydroxide. Dilute to the mark and mix thoroughly. Filter through a dry filter until exactly 250 ml. of filtrate is obtained. Dilute this to 500 ml., heat to boiling, and add 20-30 ml. of 1 per cent alcoholic dimethylglyoxime solution and stir well. Allow to stand for 30 minutes, filter through ashless paper, and ignite to nickel oxide as described above.

Since this method is not widely used, some doubt may be raised as to its accuracy and usefulness.

A procedure in which the iron is reduced to the ferrous state has been used by Balz.<sup>102</sup> Many procedures have been reported for determining nickel in ferrous materials, and in iron or steel;<sup>111-121,285</sup> in iron ore;<sup>122</sup> and in meteoric iron.<sup>123</sup>

**Determination of nickel in the presence of aluminum and chromium.** Aluminum and chromium, like iron, are normally precipitated under the conditions employed in the gravimetric determination of nickel, but as with iron the presence of tartrate prevents the formation of insoluble aluminum and chromium compounds through the formation of very stable complex ions. The procedure is entirely similar to that described above in the section on iron.

Tykrov and Lopshina<sup>124</sup> have reported a method for determining small quantities of nickel in duralumin alloys. This procedure is carried out as follows:

**Procedure.** Treat 5 g. of duralumin with 50 ml. of 15 per cent potassium hydroxide solution, and after the reaction subsides, add an additional 50-70 ml. of the potassium hydroxide solution. When hydrogen is no longer evolved, boil the mixture for 2 minutes, filter, and wash the residue (which contains nickel, copper and other metals) with hot water. Dissolve the residue in 20 ml. hot 6 N hydrochloric acid and 5 ml. of hydrogen peroxide. Filter and wash this residue, which should contain no nickel. Boil the filtrate to expel chlorine, and precipitate nickel with dimethylglyoxime in a nearly neutral solution containing tartaric acid.

A number of methods have been proposed for determining nickel in aluminum and aluminum alloys, and for the separation of nickel and aluminum.<sup>124-128</sup> Scott<sup>129</sup> has also reported a method for determining nickel in chromium-nickel steel.

**Determination of nickel in presence of cobalt.** Since the compound formed when dimethylglyoxime reacts with solutions of cobalt salts is soluble in water, nickel and cobalt may be very conveniently separated from one another. However, in the precipitation of nickel in the presence of cobalt it is necessary to add a sufficient quantity of dimethylglyoxime to combine with all cobalt to insure complete precipitation of nickel. After a time an insoluble compound of cobalt containing dimethylglyoxime and ammonia may separate from the ammoniacal solution in which the nickel precipitation is carried out, but this presents no serious difficulty since this compound is readily soluble in hot water.

It is possible to separate and determine small quantities of nickel which usually occur in cobalt salts, but the precipitation must be made from a solution buffered with acetate since nickel is only incompletely precipitated from ammoniacal solutions containing large quantities of cobalt.<sup>180-182</sup>

The precipitation of cobalt from a mixture of iron and nickel is relatively simple, but the precipitation of nickel in the presence of much cobalt is complicated by the stability of the cobalt dimethylglyoxime complex, which tends to make the precipitation of the nickel incomplete. Further, the cobalt dimethylglyoxime complex partially peptizes the nickel precipitate, making the filtration of this compound very difficult. In the presence of iron the difficulties of precipitation are enhanced by the fact that iron and cobalt together form a black precipitate with dimethylglyoxime. The initial precipitation of iron with ammonium hydroxide or zinc oxide results in a partial co-precipitation of cobalt and nickel, and this condition is not corrected by a single reprecipitation.<sup>107</sup> A more satisfactory procedure is based upon the series of reactions described by Feigl and Kapulitzas,<sup>24</sup> which is similar to that described in the section on the detection of nickel in the presence of cobalt (page 168). Cobalt is first converted to the cobaltcyanide complex by the action of potassium cyanide and hydrogen peroxide, which oxidizes cobalt to the trivalent state. By the addition of formaldehyde, the nickel cyanide complex is destroyed while the cobaltcyanide complex remains unchanged. The nickel ion is set free by the destruction of the cyanide complex and is then precipitated with dimethylglyoxime. Feigl and Kapulitzas<sup>24</sup> recommend the use of solid dimethylglyoxime rather than an alcoholic solution as the precipitant, and they then remove the solid reagent which necessarily accompanies the precipitate by dissolving in acid, and reprecipitating in the usual manner. This preference for the solid reagent may be due to the fact that potassium cobaltcyanide may be precipitated by the addition of alcohol. This method is particularly useful for separating cobalt and nickel, since any iron, which may also be present, is converted to ferricyanide which is not decomposed by formaldehyde; hence, no especial provision must be made for possible interference by iron. The following procedure is recommended:

**Procedure.** Add a saturated solution of potassium cyanide to the solution containing cobalt and nickel until the precipitate which first forms is redissolved. Then add a little 3 per cent hydrogen peroxide and heat for a few minutes. The solution should be bright yellow in color, and if it is not, again add hydrogen peroxide and heat. Evaporate the solution to about one fourth of its original volume to remove excess hydrogen peroxide. In some cases a precipitate forms during the evaporation, and if this does not dissolve in a little additional potassium cyanide it is filtered off and discarded. Dilute the clear solution to 200-300 ml. and add an excess of solid dimethylglyoxime. Warm the mixture to 50-60° C., and add formaldehyde until the odor of the latter persists. Allow the mixture to stand for 1.5 hours and filter. The residue consists of nickel dimethylglyoxime and the excess solid dimethylglyoxime. Dissolve the precipitate in dilute hydrochloric acid, filter, and precipitate nickel from the clear filtrate in the usual manner, using a 1 per cent solution of dimethylglyoxime.

For the determination of nickel in cobalt salts, where the amount of cobalt is very great, the following modification of the above procedure is used: Dissolve

15-20 g. of cobalt salt in the least possible amount of water and treat with potassium cyanide, hydrogen peroxide and formaldehyde as in the above procedure, but instead of evaporating the solution to one fourth its original volume, continue the evaporation until the mixture is thick and viscous. Then add an excess of solid dimethylglyoxime and formaldehyde and proceed as above.

The following procedure has been recommended by Evans.<sup>106</sup>

**Procedure.** First remove any iron, and then add to the solution containing both nickel and cobalt 20 ml. of 20 per cent ammonium chloride, an excess of ammonia, 5 ml. of 10 per cent sodium cyanide, and a few drops of hydrogen peroxide. Boil the mixture for 5 minutes to convert cobalt to the cobalticyanide, cool slightly, and add 10 ml. of 1:1 ammonium hydroxide solution, and then 10 ml. of 20 volume hydrogen peroxide. Boil the mixture gently for 10 minutes, and add a little more ammonia and 0.5 g. of solid dimethylglyoxime. Boil again for 1-2 minutes and allow to cool. When the mixture is cold, filter, and wash the precipitate with cold water. The nickel contained in the precipitate may be determined by any of the usual methods, but the recommended method is to dissolve in acid and determine by the cyanide titration.

**Determination of nickel in the presence of both iron and cobalt.** Nickel may be separated satisfactorily from either iron or cobalt by the procedures described above, but when both iron and cobalt are present in the same solution, together with nickel, a voluminous, amorphous red-brown precipitate is formed, even in the presence of tartaric acid.<sup>73,74,97,98,133-135</sup> Due to the physical characteristics of this precipitate, it rapidly closes the pores of the filter and can not be removed by washing. The composition of this compound is represented by the formulas,  $\text{FeCoC}_{12}\text{H}_{19}\text{N}_6\text{O}_6$ .<sup>74,134</sup> Ferrous iron and cobalt together yield no such precipitate, and so a clean separation of nickel from these two metals may easily be made by first reducing the iron before the precipitation of nickel with dimethylglyoxime. The reduction is usually effected by means of sulfur dioxide or of a sulfite, and the precipitation is carried out either in the presence of tartrate and ammonia or in an acetate buffered solution.

A number of the newer magnetic alloy steels contain cobalt, cobalt and aluminum, and cobalt, aluminum and copper. Balz<sup>102,136</sup> has applied the dimethylglyoxime method to the determination of nickel in these alloys. He has found that the separation of nickel based on the reduction of iron to the ferrous state is quite satisfactory, but in the presence of copper the precipitation must be made from an acetate solution, since in an ammoniacal tartrate solution the sulfite reduces copper to insoluble cuprous oxide or metallic copper. In an acetate buffered solution, however, this precipitation does not occur. If the alloy contains copper but no cobalt, the precipitation can then be made without the preliminary reduction. In the following procedure, which is recommended by Balz, copper and iron are first reduced by means of sulfite, and nickel is then precipitated from a solution containing tartrate. If copper is absent, the precipitation is made from an ammoniacal solution, but if copper is present the precipitation is made from a buffered acetate solution.

**Procedure.** Dissolve the sample containing about 30 mg. of nickel in 1:1 nitric acid. About 50 ml. of this acid is required for each 1 g. of the sample. Boil to expel the oxides of nitrogen and then filter to remove silica. Add 10 g. of sodium sulfite or 20 ml. of a saturated solution of sulfur dioxide for each gram of the sample taken to reduce the iron. Add 4 g. of tartaric acid for each gram of the sample and just neutralize with ammonium hydroxide. Acidify slightly by adding 1 ml. of hydrochloric acid, and dilute to 300 ml. Heat just to boiling, add 6-8 ml. of a 1 per cent alcoholic or acetone solution of dimethylglyoxime for each 10 mg. of nickel present, and precipitate nickel by the addition of 4 g. of sodium acetate. Heat gently for a few minutes and test for completeness of precipitation with an additional quantity of sodium acetate and dimethylglyoxime. Cool for 1 hour, and make certain that during this interval an excess of the reducing agent is present. Add more sulfite if necessary. Filter through a Gooch crucible, wash the residue with cold water, dry at 120° C., and weigh. If copper is absent, precipitation may be made from an ammoniacal solution, but this is unnecessary since satisfactory results are obtained in either case. The factor for nickel is 0.2032.

The reliability of this method when applied to steels containing cobalt and nickel, or cobalt, copper and nickel, is shown by the results given in Table 32, which is taken from the work of Balz:

TABLE 32.

Composition of Alloy	Nickel Found	Precipitation
1. Nickel .....23.6 per cent	23.57 per cent	From acetate solution
Aluminum .... 5.8 per cent	23.59 per cent	From acetate solution
Cobalt ..... 3.5 per cent	23.58 per cent	From ammoniacal solution
Iron .....Remainder	23.56 per cent	From ammoniacal solution
2. Nickel .....20.3 per cent	20.29 per cent	From acetate solution
Cobalt .....10.8 per cent	20.26 per cent	From acetate solution
Aluminum .... 7.3 per cent	20.28 per cent	From acetate solution
Copper ..... 5.8 per cent		
Iron .....Remainder		

**Determination of nickel in presence of copper.** Since copper hydroxide, which is formed when ammonium hydroxide is added to a solution of a copper salt, is soluble in an excess of ammonia, it might appear that copper would not interfere with the determination of nickel by precipitation with dimethylglyoxime from an ammoniacal solution. Under these conditions, however, some copper is co-precipitated with nickel, and not all copper is dissolved by the excess of ammonia. Consequently results obtained by precipitating nickel in the presence of copper from an ammoniacal solution are not reliable.<sup>90,187</sup> Precipitation from a solution buffered with acetate appears to give a satisfactory separation, but this problem has not been sufficiently studied to justify definite conclusions.<sup>187</sup> Balz,<sup>102,186</sup> as we have seen, reports that such separation is satisfactory in the presence of tartrate, but Grossmann and Mannheim<sup>90</sup> report that a little copper



is always carried down mechanically with a nickel precipitate, and that a second precipitation is necessary to obtain a satisfactory separation. Because of this uncertainty, the better procedure to follow is that described above in which copper is first reduced to the cuprous state before precipitation with dimethylglyoxime in the solution containing tartrate and buffered with acetate.<sup>102,136,138</sup>

Various procedures have been suggested in which copper is removed before determining nickel with dimethylglyoxime.<sup>139</sup> Vodret and Gallo,<sup>140</sup> for example, precipitate copper in an acid solution as copper sulfide by adding sodium thiosulfate; and, after filtration, determine nickel in the filtrate with dimethylglyoxime. Halls<sup>141</sup> has recommended removing copper electrolytically before precipitating nickel with dimethylglyoxime.

**Determination of nickel in the presence of zinc.** No difficulty is encountered in the precipitation of nickel from an ammoniacal solution containing zinc,<sup>71,110</sup> or from an acetate buffered solution containing zinc.<sup>142</sup> The following procedure has been reported by Cockburn, Gardiner and Black.<sup>142</sup>

**Procedure.** Neutralize the solution to be analyzed with ammonium hydroxide, and make just acid with dilute hydrochloric acid. Add a 1 per cent alcoholic solution of dimethylglyoxime in a quantity equal to 7 times that of the nickel present, and then add a few ml. of 10 per cent sodium acetate. Heat to boiling for one-half hour, filter through a Gooch crucible, wash with hot water, dry at 110° C. and weigh. The factor for nickel is 0.2032.

The author recommends filtering the precipitate from a hot solution and washing with hot water, although this procedure is not generally regarded as satisfactory.

Some procedures call for the precipitation of zinc as zinc sulfide before precipitating nickel with dimethylglyoxime. When the precipitation of the sulfide is made from a solution containing chloroacetic acid, this reagent interferes with the subsequent precipitation of nickel with dimethylglyoxime. This interference can be eliminated by boiling for 15 minutes, during which 60 ml. of saturated sulfur dioxide solution is added in small portions.<sup>143</sup>

**Determination of nickel in presence of manganese.** Small quantities of manganese, such as are commonly present in iron or steel, cause no difficulty in the separation of nickel by precipitating with dimethylglyoxime from an ammoniacal tartrate solution; but when larger quantities of manganese are present, as in certain alloys, the precipitation must be made from a solution buffered with acetate.<sup>144</sup> Kundert<sup>41</sup> has described a method for the determination of nickel in manganese ores.

**Determination of nickel in brass, bronze and other alloys.** Nickel may be determined in many alloys by procedures which have been specially designed to prevent interference by the various metals which may be present.

Alloys for which procedures employing dimethylglyoxime for the determination of nickel have been reported are: brass;<sup>145,146</sup> bronze;<sup>147</sup> dental alloys;<sup>149</sup> copper alloys containing antimony and nickel;<sup>150</sup> brass, alloyed with manganese;<sup>144</sup> copper alloys containing nickel and aluminum;<sup>151</sup> and in nickel-aluminum

alloys.<sup>148</sup> These alloys are listed in addition to those which are included in above sections devoted to interference caused by particular elements.

**Determination of nickel in presence of vanadium.** Nickel may be precipitated by dimethylglyoxime in the presence of vanadium if the latter is first oxidized to vanadic acid by boiling with nitric acid. The following procedure for determining nickel in ferrovanadium is taken from the work of Schilling.<sup>152</sup>

**Procedure.** Dissolve 1 g. of very finely divided ferrovanadium in 30 ml. of hydrochloric acid, oxidize by the addition of nitric acid, evaporate to dryness, and then heat strongly until the nitrate is decomposed. Cool and dissolve the oxides in cold hydrochloric acid. Filter off the silica, and wash the residue with hot dilute hydrochloric acid. To the filtrate, add 20 ml. of 1:5 acetic acid and make slightly alkaline with ammonium hydroxide. Precipitate nickel with a 1 per cent alcoholic solution of dimethylglyoxime. Allow to stand for a short time and filter. Wash with hot water until free of iron, and then heat to constant weight at 110° C. The dry precipitate contains 20.32 per cent nickel and is free from vanadium.

**Determination of nickel in the presence of tungsten.** Fettweis<sup>153</sup> has attempted to determine nickel in tungsten steels by precipitating with dimethylglyoxime, but he has found that the nickel precipitate invariably retains some tungstic oxide and that the nickel results are from 0.05-0.1 per cent too high.

**Determination of nickel in silicate rocks.** The determination of very small quantities of nickel in silicate rocks is best accomplished by means of a colorimetric method; although a gravimetric procedure, based upon the precipitation of nickel with dimethylglyoxime, has been used by Harwood and Theobald.<sup>52</sup> Their procedure is as follows:

**Procedure.** Place 2 g. of the finely powdered rock to be analyzed in a platinum dish and digest with 15 ml. of concentrated sulfuric acid and 20-25 ml. of pure hydrofluoric acid. Heat the mixture on a sand bath with frequent stirring with a heavy platinum wire for the first 20 minutes. When all action has ceased,<sup>9</sup> add a crystal of potassium nitrate and evaporate until dense fumes appear. Continue to heat for about 10 minutes and then cool. Add sufficient water to dissolve all soluble material, and again evaporate until the mixture fumes. Cool, add 100 ml. of water and again heat until all soluble salts have passed into solution. Filter if necessary, and add 2-3 g. of citric acid, and then add sodium hydroxide until the mixture is neutral to methyl red. Now make very slightly acid with a few drops of sulfuric acid, add 15 ml. of a 1 per cent alcoholic solution of dimethylglyoxime. and make slightly alkaline with 4 N ammonium hydroxide. Allow to stand for 24 hours and filter. Wash with cold water. Dissolve the precipitate in a little hot 7.5 N nitric acid and add a few drops of concentrated sulfuric acid. Evaporate on a water-bath as long as any of the material volatilizes. Dissolve the residue in water, filtering if necessary, and add 10 mg. of citric acid and 5-7 ml. of 1 per cent alcoholic solution of dimethylglyoxime. Again make barely alkaline with ammonium hydroxide.

Allow to stand overnight and filter. Wash free from sulfate, dry at 120-130° C., and weigh.

As little as 0.0025 per cent of nickel can be determined by this procedure. If the rock contains more than 0.05 per cent NiO, it is best to determine the nickel content of the aluminum oxide precipitate, or else make a determination of the nickel content of the filtrate after removing magnesium. This value should then be subtracted from the total nickel content, and gives the nickel adsorbed by the aluminum precipitate.

**Colorimetric determination of nickel.** Very small quantities of nickel can be determined colorimetrically by comparing the color formed when dimethylglyoxime is added to extremely dilute solutions of nickel salts with that obtained with nickel solutions of known concentration. Due to the extremely low solubility of nickel dimethylglyoxime, only minute quantities of nickel can be determined in this way.<sup>131,154-156</sup> The following procedure illustrates this method:

**Reagent.** Dissolve 1.2 g. of dimethylglyoxime in 100 ml. of 95 per cent alcohol.

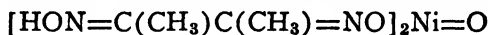
**Procedure.** Dissolve the material to be analyzed in water and add 2-3 ml. of concentrated nitric acid. Boil for a few minutes, and add an excess of 6 N ammonium hydroxide to precipitate any iron or phosphate. Filter, and dissolve the precipitate in dilute hydrochloric acid, and again precipitate with ammonium hydroxide. Filter, and wash, and repeat the precipitation if much iron is present. Combine the filtrates and evaporate to dryness, and dissolve the residue in 5 ml. of 6 N hydrochloric acid. Dilute to 100 ml., heat to boiling, and treat the hot solution with hydrogen sulfide. Filter, expel hydrogen sulfide from the filtrate by boiling, and precipitate nickel with 6 N sodium hydroxide. Filter, dissolve the nickel hydroxide in a slight excess of 6 N hydrochloric acid and dilute to a definite volume. Mix thoroughly, and to the solution, or an aliquot part of it, add a slight excess of ammonium hydroxide and 2 ml. of the reagent solution. Mix well and compare the resulting color with that of a standard nickel solution prepared simultaneously.

Ochotin and Siuchov<sup>154</sup> recommend extracting the colored complex with ether for determining nickel in alloys:

**Procedure.** Dissolve 10-15 mg. of the alloy to be analyzed in 10 ml. of concentrated nitric acid, and dilute with water to 25 ml. Then add ammonium hydroxide in sufficient quantity to form the blue complexes of copper and nickel. Heat the mixture, and add 15 ml. of a 1 per cent alcoholic solution of dimethylglyoxime. Transfer the mixture to a separatory funnel. Cool quickly with running water, add 15 ml. of ether, and shake well. Drain off the aqueous solution from the ether extract of the nickel precipitate, and wash the latter two times with water. Transfer to a color comparison tube containing 5 ml. of ethyl alcohol and 5 ml. of collodion. Dilute to the mark with ether and compare with standards similarly treated.

A complete analysis using this method requires less than 10 minutes, and in this way 0.1-0.2 mg. of nickel can be determined with an accuracy about 1 per cent.

The effect of oxidizing agents in preventing the precipitation of nickel with dimethylglyoxime has been mentioned in an earlier section (page 174). Nitrate, ferricyanide, permanganate, and in general all oxidizing agents, have the effect of preventing the precipitation of nickel dimethylglyoxime, and cause the formation of an intense red solution, which contains a soluble complex of tetravalent nickel. According to Feigl,<sup>64</sup> this complex has the structure



This reaction has been used as an excellent means for the colorimetric determination of small quantities of nickel. Rollet,<sup>65</sup> who was the first to attempt the determination of nickel by this reaction, used bromine as the oxidizing agent. An excess of bromine water, which is recognized by the yellow color of the solution, must be added to ensure complete oxidation of the nickel, and therefore complete color development. Ammonium hydroxide is then added to remove the excess bromine and adjust the pH of the solution.

The hue and color intensity of the solution of the nickel complex depend upon the original acidity of the nickel solution. If bromine water is added to the solution and is followed by ammonium hydroxide and dimethylglyoxime, a brownish solution is obtained, but if the bromine is added to a neutral or slightly ammoniacal solution, and the solution then made ammoniacal if previously neutral, a wine-red color is formed. The color intensity is stronger in solutions which are initially ammoniacal or neutral. A variation in the acidity of the sample solution ranging from 0.25 to 0.5 N in hydrochloric acid, however, is without effect on the color intensity.

The following procedure is recommended by Mitchell and Mellon:<sup>286</sup>

**Procedure.** Dissolve by suitable means a quantity of the material to be analyzed which contains not more than 0.5 mg. of nickel. Make the solution just acid by means of hydrochloric acid or ammonium hydroxide, as necessary. Add bromine water dropwise until the solution is a faint yellow, and then add 2 ml. in excess. Then add 10 ml. of concentrated ammonium hydroxide. If a precipitate forms, stir well and filter. Collect the filtrate in a 100-ml. volumetric flask. If no precipitate forms, omit the remainder of the separation procedure. Dissolve any precipitate in the smallest quantity of 1:1 hydrochloric acid, and reprecipitate by adding 1 ml. of bromine water and 4 ml. of concentrated ammonium hydroxide. Filter, wash, and add the second filtrate to the first. To the combined filtrates, add 35 ml. of 95 per cent ethyl alcohol and 20 ml. of a 0.1 per cent alcoholic solution of dimethylglyoxime. Dilute to volume, mix well, and measure by suitable means. A filter such as Corning No. 440 Signal green is recommended for filter photometers.

The following ions do not interfere in concentrations 300 times that of nickel: acetate, arsenate, arsenite, benzoate, borate, bromide, carbonate, chloride, citrate, cyanide, fluoride, formate, iodate, lactate, molybdate, nitrate, nitrite,

oxalate, perchlorate, periodate, orthophosphate, pyrophosphate, sulfate, sulfite, tartrate, tungstate, lithium, potassium and sodium.

The following ions precipitate and must be removed unless their interference can be eliminated by the formation of complexes or by other suitable means: chlorostannous, chlorostannic, iodide, permanganate, silicate, thiosulfate, vanadate, aluminum, antimony, barium, beryllium, bismuth, cerium, chromium, copper, ferrous, ferric, lead, magnesium, manganese, mercuric, mercurous, platinum, silver, strontium, thorium, titanium, uranyl and zirconium.

Auric, cobaltous and dichromate ions interfere because of their color. Other ions which interfere are cadmium, calcium, chlorate, selenate, thiocyanate and zinc. The extent of this interference is shown in Table 33:

TABLE 33.—EFFECT OF IONS ON THE DETERMINATION OF NICKEL

Ion	Amount Permissible p.p.m.	Error Per Cent
$\text{ClO}_3^-$	600	2
$\text{Cr}_2\text{O}_7^{2-}$	5	4
$\text{SeO}_4^{2-}$	100	2.5
$\text{SCN}^-$	400	1
$\text{Au}^{+3}$	20	2.5
$\text{Cd}^{+2}$	600	0.5
$\text{Ca}^{+2}$	100	1
$\text{Co}^{+2}$	10	1
$\text{Zn}^{+2}$	600	0.5

In the absence of interfering substances, the method is accurate to about 5 per cent within the limits 0.001-0.01 mg. of nickel per ml. of solution. The accuracy is greater with larger quantities of nickel.

According to Fairhall,<sup>302</sup> this method is only roughly quantitative. He reports that the color is caused by crystalline particles of the nickel oxime, and that the method is actually turbidimetric rather than colorimetric. Since particle size may vary depending upon the conditions of formation, a more rigid control is required than in colorimetric methods. Despite these claims, however, the dimethylglyoxime method has been successfully applied to the determination of small quantities of metal in aluminum alloys,<sup>280,281,283,288,299</sup> copper-base alloys,<sup>289,299,301</sup> iron ore,<sup>155</sup> silicate rocks,<sup>163</sup> steel,<sup>157,158,160,161,278,287,290,292,299,301</sup> electroplating baths,<sup>277</sup> alloys<sup>293</sup> and bronze.<sup>279</sup>

Hummon<sup>292</sup> has used the following method for the determination of nickel in steel, in which ammonium persulfate is used as the oxidizing agent:

**Procedure.** Dissolve 0.5 g. of steel in 15 ml. of 5 N nitric acid, and heat to remove the oxides of nitrogen. Boil slowly for 15 seconds with 10 ml. of a solution prepared by dissolving 10 g. of ammonium persulfate in 50 ml. of water. Dilute with 1 ml. of methyl alcohol and 10 ml. of water. Add 25 ml. of concentrated ammonium hydroxide, boil for 1 minute, and cool to room temperature. Then add 10 ml. of concentrated ammonium hydroxide, 10 ml.

of the ammonium persulfate solution, and 5 ml. of a 1 per cent alcoholic solution of dimethylglyoxime. Shake well after each addition. Transfer the mixture to a 200-ml. volumetric flask, mix well, and dilute to the mark. Filter through a Whatman 41 filter paper, and discard the first 10 ml. of the filtrate. Read in a photoelectric colorimeter.

Small quantities of nickel, especially in the presence of a large excess of iron and other common metals, may be determined by precipitating as nickel dimethylglyoxime from an ammoniacal citrate solution of the prepared sample, then dissolving the precipitate in pyridine and comparing the color produced with that of a pyridine solution containing a known quantity of nickel dimethylglyoxime.<sup>284</sup>

**Determination of nickel in steel.** Various procedures have been proposed for the colorimetric determination of small quantities of nickel in steel.<sup>157,158,160,161,278,282,287,290-292,299,301,303</sup> The following method, described by Sandell,<sup>308</sup> is based on the procedure of Murray and Ashley:<sup>160</sup>

**Procedure.** Dissolve 0.50 g. of steel in 10 ml. of warm 1:1 nitric acid. Boil to remove the oxides of nitrogen and cool. Dilute to 250 ml. with water and mix well. Allow to stand until any insoluble material has settled, and transfer 5 ml. of the clear solution to a 50-ml. volumetric flask. To this solution add, in the following order, and with mixing after each addition, 5 ml. of 10 per cent citric acid solution, 2 ml. of saturated bromine water, 2 ml. of 1:1 ammonium hydroxide solution, and 1 ml. of 1 per cent alcoholic dimethylglyoxime solution. Dilute to the mark with water and mix thoroughly. Determine the transmittancy of the solution within 10 minutes, using a green filter with mean transmission at 530  $m\mu$ . The nickel solutions used for preparing the standard curve should contain the same concentration of nickel-free iron as the sample solution.

Makepeace and Craft<sup>278</sup> have described a modification of the method of Murray and Ashley,<sup>160</sup> which they claim gives a highly stable and readily reproducible red color, and which is particularly suitable for routine work because of its rapidity and manipulative simplicity. Copper and cobalt interfere only slightly, and other elements commonly found in steel do not interfere. The accuracy of this method is comparable to that of routine gravimetric procedures.

**Procedure.** Decompose a 0.25 g. sample of steel in 20 ml. of a solution containing 133 ml. of sulfuric acid ( $d = 1.82$ ) and 167 ml. of orthophosphoric acid per liter. Steels containing little chromium may be dissolved directly in 8 N nitric acid. It may be necessary to use hydrochloric acid with stainless steels. Carefully add 10 ml. of 8 N nitric acid and boil to expel the oxides of nitrogen. Transfer the solution to a volumetric flask of suitable size and dilute to the mark. Transfer to a 100-ml. volumetric flask an aliquot containing between 0.05 and 0.3 mg. of nickel. To this add, in the following order, and with mixing after each addition, 5 ml. of 20 per cent tartaric acid solution, 5 ml. of saturated bromine water, 10 ml. of ammonium hydroxide ( $d = 0.90$ ), and 5 ml. of a 1 per cent solution of dimethylglyoxime in methyl alcohol. Allow to stand 1 minute and add 10 ml. of 6 N sodium hydroxide solution, and then dilute to

the mark. After 5 minutes, transfer the solution to the optical cell of a spectrophotometer and compare the transmittance at 530  $m\mu$  with that of pure water.

In some cases, the color of the solution fades upon the addition of sodium hydroxide, due to the use of impure or partially decomposed tartaric acid or dimethylglyoxime. This difficulty can be overcome by the addition of a second 5-ml. portion of bromine water after the introduction of the dimethylglyoxime.

Impure dimethylglyoxime may be made suitable for use by acidifying the alcoholic solution with dilute sulfuric acid and adding sufficient bromine water to impart to it a yellow color. This should be done 15-30 minutes before use. Additional small quantities of bromine water may be needed from time to time to keep the solution yellow. Do not use the treated reagent after a few hours.

The colorimetric method has been used for determining quantities of nickel ranging up to 15 per cent in steel, using the Leifo photometer<sup>158,159</sup> and the Zeiss-Pulfrich step photometer.<sup>160</sup> For high concentrations of nickel it is necessary to carry out the color comparison with aliquots of large samples, but the results appear to be very satisfactory. These methods represent an important contribution in steel analysis, because of the speed with which they can be carried out.

Korenman and Voronov<sup>161</sup> suggest the following procedure:

**Procedure.** Dissolve 0.2-1.0 g. of the steel or cast iron to be analyzed in nitric acid and heat to boiling. Cool, dilute to 200 ml., and filter. Add 5-25 ml. of 25 per cent Rochelle salt, 5 ml. of saturated bromine water, 2 ml. of 25 per cent ammonia, and 3 ml. of 1 per cent alcoholic dimethylglyoxime to 5-25 ml. portions of the test and standard solutions. Compare in a colorimeter after 5 minutes.

Fedorov and Yanovskii<sup>162</sup> have used this method for the determination of nickel in slags.

**Colorimetric determination of nickel in silicate rocks.** Sandell and Perlich<sup>163</sup> have developed a colorimetric procedure for the determination of nickel in silicate rocks. This method is based upon the extraction of nickel dimethylglyoxime with chloroform from the ammoniacal citrate solution of the rock sample. By shaking the chloroform extract with dilute hydrochloric acid, nickel dimethylglyoxime is decomposed and the aqueous solution of nickel is then determined colorimetrically by Rollet's method. This method is particularly well suited for the analysis of rocks having such low nickel content that the gravimetric procedure of Harwood and Theobald<sup>52</sup> cannot be used.

The following procedure is taken from the work of Sandell and Perlich:<sup>163</sup>

**Procedure.** Weigh 0.25 g. of finely powdered basic rock containing 0.01-0.05 per cent nickel, or 0.5 g. or more of acidic rock, into a platinum dish. Add a few ml. of water, 0.5 ml. of 70 per cent perchloric acid, and 2.5 ml. of hydrofluoric acid. If it is necessary to weigh samples larger than those indicated above, the amounts of reagents added should be proportionately increased. Evaporate the mixture to dryness, dissolve the residue in 0.5 ml. of perchloric

acid and 2-3 ml. of water, and again evaporate to dryness. To the residue add 0.5-1.0 ml. of concentrated hydrochloric acid and 5 ml. of water. Heat the mixture until all soluble material has passed into solution, and add 5 ml. of 10 per cent sodium citrate solution. Cool, and add concentrated ammonium hydroxide dropwise until the mixture is alkaline to litmus, and then add a few drops in excess. Filter through a small paper if the quantity of precipitate formed is appreciable. Wash the residue with several small portions of water, and ignite the paper and contents. Fuse the residue with about 0.1 g. of sodium carbonate, cool, and add an excess of dilute hydrochloric acid, and then heat until all soluble material is dissolved. Add 2-3 ml. of 10 per cent sodium citrate solution, and then add ammonium hydroxide until the mixture is slightly alkaline. At this point there are two solutions to be used in further steps in the analysis: (1) the principal filtrate from the insoluble material; and (2) the ammoniacal solution of the sodium carbonate fusion mixture.

To the filtrate from the insoluble material add 2 ml. of 1 per cent alcoholic dimethylglyoxime solution, and shake vigorously for 30 seconds with three 2-3-ml. portions of reagent quality chloroform. Extract the ammoniacal solution of the sodium carbonate, melt in a similar manner. Combine all the chloroform extracts, and shake vigorously with 10 ml. of 1:50 ammonium hydroxide solution. Place the mixture in a separatory funnel and carefully draw off the chloroform layer so that none of the aqueous phase accompanies it, then shake the aqueous layer with 1-2 ml. of chloroform in order to recover any of the chloroform solution which remains suspended in it. Now decompose the nickel dimethylglyoxime contained in the chloroform solution by vigorously shaking the chloroform solution for 1 minute with two 0.5-ml. portions of 0.5 N hydrochloric acid. Carefully separate the hydrochloric acid solution and transfer to a volumetric flask of suitable size, or to a flat-bottomed color comparison tube ( $1.8 \times 15$  cm.). No appreciable quantity of chloroform should be transferred with the hydrochloric acid solution. If a colorimeter is used for the color comparison, the concentration of nickel in the final solution should be at least 0.001 mg. per ml. For most acid rocks a colorimeter can not be used because of the low nickel content, and a standard series of color comparison tubes must be employed. For a 0.5 g. sample of an acid rock, a suitable series may range from 0.000 to 0.001, 0.002, 0.003, . . . . 0.010 mg. of nickel. Regardless of which method is used, colorimeter or tubes, the final concentration of the nickel should not exceed 0.005 mg. per ml., since otherwise nickel dimethylglyoxime may be precipitated.

The final color comparison is made as follows: Dilute the unknown nickel solution and the standard nickel solution which is to be used in the comparison to about 10 ml. with 0.5 N hydrochloric acid. To each add 5 drops of freshly prepared saturated bromine water and mix, and then add concentrated ammonium hydroxide dropwise with shaking until the color of bromine disappears, and finally add 3 or 4 drops in excess. Then add 0.5 ml. of 1 per cent alcoholic solution of dimethylglyoxime, mix, and dilute to volume with water if the solution is contained in a volumetric flask. Make the color comparison immediately. The color intensity of the solution increases slowly on standing, and for this reason the unknown and the standard solution should be treated



with the same reagent simultaneously. If necessary, apply a correction for the nickel contained in the reagents.

The sensitivity of this method is great enough to permit detection of less than 0.0001 per cent of nickel when a 0.5 g. sample of rock is used. Excellent results have been reported with samples ranging in nickel content from 0.0003 to 0.04 per cent. Under the conditions outlined for the final nickel determination, the color intensity follows Beer's law closely for nickel concentrations ranging up to approximately 0.006 mg. of nickel per ml. For concentrations greater than this precipitation may occur.

Copper, manganese, chromium, cobalt and vanadium in quantities which usually occur in most igneous rocks do not interfere. Copper and cobalt, if present in appreciable quantities, cause high results. In a special investigation to determine the effect of cobalt and copper on this determination, 0.1 mg. of cobalt was carried through the procedure and gave a color corresponding to about 0.0015 mg. of nickel, although 0.100 mg. of copper gave no color. High concentration of manganese may cause trouble by oxidizing nickel in the ammoniacal solution during the shaking, and this results in a loss of nickel because the nickelic dimethylglyoxime is not soluble in chloroform.

**Titrimetric determination of nickel.** A number of titrimetric methods using dimethylglyoxime have been proposed for the determination of nickel. Three general methods are used for this purpose. These are based on the following principles: (a) nickel may be precipitated with a standard solution of dimethylglyoxime, using a suitable means for observing the end-point of the titration; (b) the formation of one molecule of nickel dimethylglyoxime is accompanied by the liberation of 2 hydrogen ions, and nickel may thus be determined indirectly by titration of the acid liberated in this reaction; (c) when a precipitate of nickel dimethylglyoxime is decomposed by treatment with hot acid, hydroxylamine is formed, and the estimation of this compound gives an indirect measure of the nickel content of the precipitate.

**The titration of nickel with dimethylglyoxime solution.** Nickel may be determined titrimetrically by a method based upon Brunck's reaction in which 2 moles of dimethylglyoxime precipitate quantitatively 1 mole of nickel in a slightly ammoniacal solution. Various modifications of this procedure have been proposed, but these differ essentially in the method used to determine the end-point of the titration. The following method has been used by Belasio and Marchionneschi<sup>164</sup> for the determination of nickel in argentan, nickeliferous bronzes and brasses and in nickel steel:

**Standard solution of dimethylglyoxime.** Dissolve 1.582 g. of pure dimethylglyoxime in 1500 ml. of 95 per cent alcohol and dilute to 2 liters with water. One ml. of this solution corresponds to 0.2 mg. of nickel.

**Procedure.** The solution to be analyzed should be diluted to contain about 0.5 per cent nickel, and may contain zinc and very small quantities of iron, manganese, aluminum and lead. Make this solution slightly alkaline with ammonium hydroxide, and determine in an aliquot the approximate volume of

the standard solution necessary to precipitate all the nickel. This is determined by adding the reagent until the red precipitate does not visibly increase in quantity, and then allowing a drop of the titration mixture to fall on a piece of doubly-folded filter paper. The upper fold retains the precipitate; and if on touching the spot on the second fold with a little of the dimethylglyoxime solution, the red color no longer develops, the nickel may be assumed to be completely precipitated. Filter the solution, and add more reagent. Only a very light red color should appear.

To aliquot parts of the nickel solution having the same volume as that used in the preliminary test, add volumes of standard dimethylglyoxime solution determined as follows: assuming that the preliminary test showed that the aliquot required 9.2 ml. of the standard solution, add 9.2, 9.4, 9.6, 9.8, and 10.0 ml. respectively to different aliquots. Allow to stand for 5-10 minutes and filter these solutions into two series of test tubes which are about one-third filled. To one series add a little 1 per cent alcoholic solution of dimethylglyoxime; and to the other series add a little dilute nickel sulfate solution. Allow the mixtures to stand for 15 minutes. In the first series the end-point will be indicated in the tube in which the decreasing red color finally disappears, while in the other series the end-point will be indicated where the color first appears. The volume of the standard reagent is then indicated by the number of ml. added to the test tubes in which the end-point is indicated by the appearance or disappearance of the red color.

To determine nickel in nickeliferous bronzes and brasses and similar alloys, dissolve the material in nitric acid, cool, neutralize with ammonium hydroxide, and acidify slightly with hydrochloric acid. Then precipitate copper with tin by using twice as much tin as copper present, and finally determine nickel as described in the above procedure.

To determine nickel in steel, dissolve the material in hydrochloric acid, add nitric acid to oxidize the iron, cool, and add dilute ammonium hydroxide until the liquid remains a clear red-brown. Then precipitate the iron with ammonium acetate and sodium succinate and proceed as described above.

The above procedure is somewhat cumbersome and time consuming, and to eliminate the difficulties of this method many simpler procedures have been suggested. Ishibashi and Tetsumoto<sup>166</sup> have proposed a direct titration of nickel using an alcohol or acetone solution of dimethylglyoxime, and detecting the end-point of the titration by means of ferrous ammonium sulfate as an outside indicator. With this reagent an excess dimethylglyoxime yields a deep red color. The end-point of the titration may also be determined by using dimethylglyoxime test paper as a spot test indicator. Such paper is sensitive to 1 drop of 0.001 per cent nickel solution.<sup>166,167,275</sup>

In a recent investigation, Bogatskii, Dzyubanna, and Kosaya<sup>168</sup> have recommended precipitating nickel with a standard solution of dimethylglyoxime, and then titrating the excess reagent with a standard solution of a nickel salt. The end-point is determined by spot testing with paper which has been moistened with a nickel salt solution and another paper moistened with dimethylglyoxime solution.

Bucherer and Meier<sup>169</sup> recommend the titration of nickel by dimethylglyoxime using the filtration method of determining the end-point. By this method the end-point is attained when a little of the filtrate from the solution in which the precipitation is carried out gives no further precipitation with an added drop of the reagent. The standard dimethylglyoxime solution is prepared by dissolving 1.5 g. of dimethylglyoxime in 50 ml. of acetone and then diluting to 500 ml. with 40 per cent acetone in water. This solution may be standardized against a solution containing a known quantity of a nickel salt. The standard solution is then added dropwise from a buret to a slightly ammoniacal solution of the nickel salt until a little of the filtrate from the solution shows no further precipitation when treated with a little more of the reagent.

In a properly buffered solution it is possible to titrate a nickel solution with an alcoholic solution of dimethylglyoxime by determining the end-point by means of a conductivity curve. Results are more satisfactory in this determination when the nickel is completely precipitated by adding an excess of the standard dimethylglyoxime solution and back titrating with the standard nickel solution. The presence of cobalt, iron and copper interferes somewhat with this determination.<sup>170</sup>

Kolthoff and Langer<sup>171</sup> have titrated nickel with a dimethylglyoxime solution, using the dropping-mercury electrode as an indicator electrode. This method yields accurate and precise results for very dilute nickel solutions. Excellent results are obtained at a concentration range between 0.01 to 0.0001 molar.

**Determination of nickel based upon acid-base titration.** The formation of 1 mole of nickel dimethylglyoxime is accompanied by the liberation of 2 hydrogen ions, and a titrimetric method for the determination of nickel has been based upon the estimation of the acid liberated in this reaction.<sup>172</sup> This titration is made possible by the fact that dimethylglyoxime is practically unionized in alcohol or water; and is stable in alkali, being converted into dimethylfurazan only to a slight extent after long boiling with concentrated alkali solutions. By preparing a water-alcohol solution of dimethylglyoxime and potassium hydroxide it is possible to add the reagent and the standard base at the same time, thereby simplifying the titration. The following method has been used by Holluta.<sup>172</sup>

**Reagent.** Prepare a standard 0.02 N solution of dimethylglyoxime by dissolving 4.6400 g. of the reagent in 300-400 ml. of 97 per cent alcohol. Then add from a buret, with constant shaking, 20 ml. of 1 N potassium hydroxide solution, and dilute the mixture to 1 liter with carbon dioxide-free water. Allow to stand for 24 hours, and filter from any potassium carbonate which separates. The alcohol used in the preparation of this solution must be free of aldehydes and must be neutral in reaction. Check the alkali content of this solution by titration with a standard acid, using phenolphthalein as the indicator.

**Procedure.** Dilute the solution to be analyzed to such an extent that a suitable volume of the standard solution will be required. Add 4-8 drops of indicator, depending on the quantity of solution, and then add a 0.1 or 0.02 N

solution of potassium hydroxide to the appearance of a red color. Finally, add a few drops of hydrochloric acid of the same normality as the base until the red color disappears. Add 2-5 ml. of the standard reagent solution, and after vigorously agitating, warm gently. In this way the precipitate is coagulated into balls which adhere to the walls of the flask or float on surface of liquid leaving a clear solution. The standard solution is then gradually added with frequent shaking until solution acquires a permanent pale pink color. Because of the bulkiness of the precipitate the initial solution should not contain more than 0.03 g. of nickel.

One ml. of the reagent solution is equivalent to 0.0005869 g. of nickel.

Parr and Lundgren<sup>178</sup> have used a modification of the above procedure to determine nickel in alloys.

**Procedure.** Dissolve the nickel in a hydrochloric or nitric acid solution, and if aluminum, iron or chromium is present, add about 2 times their weight of tartaric acid to prevent precipitation. If chromium is present, add also a little ammonium chloride. If manganese or zinc is present use hydrochloric acid and evaporate until most of the free acid is removed. Iron must be oxidized to the ferric state. The amount of cobalt present must not exceed 0.1 g. per 100 ml., and an excess of the reagent must be used.

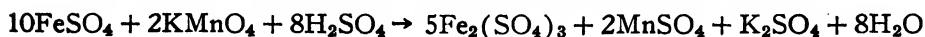
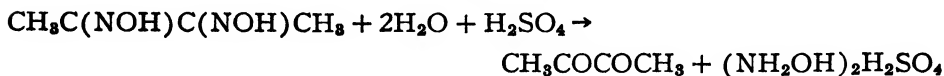
Dilute the solution to be analyzed to 300-400 ml. and neutralize any free acid with an excess of sodium acetate. Heat nearly to boiling and add 5 times as much reagent in a 1 per cent alcoholic solution as there is nickel present. Then completely neutralize the mixture with ammonium hydroxide, using a very slight excess, and heat until the red compound is precipitated. Filter and wash. Place the precipitate and filter in a beaker and add an excess of 0.05 N sulfuric acid. Dilute to 200 ml. and heat until solution is complete. Titrate with 0.1 N potassium hydroxide, using the appearance of the first yellowed tinge as the end-point. The solutions used in this procedure must be standardized against pure nickel.

Krupenio<sup>174</sup> has determined nickel ores by precipitating nickel with dimethylglyoxime, then dissolving the precipitate in an excess of standard hydrochloric acid, and back titrating with sodium hydroxide. In this way a maximum of 12-15 mg. of nickel can be determined.

**Procedure.** Fuse 1 g. of the powdered ore with 10-12 volumes of potassium persulfate, and digest the melt with 100 ml. of 2-3 per cent sulfuric acid. Boil for 10-15 minutes and filter from the residue. Add 5-8 g. of citric acid to the filtrate and heat. Add 15 ml. of 1 per cent alcoholic solution of dimethylglyoxime and an excess of ammonium hydroxide. Allow to stand overnight and filter, and wash the precipitate with hot water. Dissolve the nickel compound in 50-ml. of 0.1 N hydrochloric acid and back titrate with 0.1 N sodium hydroxide, using methyl orange as the indicator.

**Titration of nickel dimethylglyoxime.** Nickel may be determined indirectly by a method devised by Tougarinoff.<sup>175,177</sup> Nickel is first precipitated with dimethylglyoxime, and the precipitate of nickel dimethylglyoxime is then con-

verted by heating with hot dilute acids into a ketone or aldehyde and hydroxylamine. The hydroxylamine is then determined by the method of Bray, Simpson and Mackenzie,<sup>178</sup> which consists of oxidizing the hydroxylamine to nitrous oxide by boiling with an excess of ferric salt and titrating the resulting ferrous ion with potassium permanganate. The reactions occurring during this determination are represented by the following equations:



The following procedure may be used for the determination of nickel in steel:

**Procedure.** The preliminary step in this procedure consists in precipitating the nickel in a steel or non-ferrous alloy according to the usual procedure given in the section on the gravimetric determination of nickel. The sample used must be of such size that not more than 25 mg. of nickel is present. Filter the precipitate and wash well, but it is not necessary to attempt to transfer the last traces of the precipitate to the filter. Pour 15 ml. of approximately 12 N sulfuric acid into the flask in which the precipitation was carried out and heat to boiling. Make sure that all the precipitate remaining in the flask is dissolved in the acid. Pour the hot acid on to the precipitate contained in the filter and stir with a glass rod to complete solution of the precipitate. Collect the filtrate in a 300 ml. Kjeldahl flask. When all the precipitate has dissolved, make a hole in the bottom of the filter and rinse the flask and the filter with boiling water until the volume of the filtrate is about 75 ml. Now concentrate the filtrate by rapid evaporation until the volume is 25 ml. The boiling should be carried out at such rate that the concentration requires about 10 minutes. While continuing to boil the mixture, add 50 ml. of a solution containing 40 g. of ferric sulfate per liter, and allow the mixture to boil for 5 minutes longer. Cool the solution with running water, and add 150 ml. of water and 3 ml. of phosphoric acid ( $d = 1.7$ ). Then titrate with 0.1 N potassium permanganate to the appearance of a permanent pink color. The calculations are based upon the equations given above.

This method has been tested on various materials, including pure nickel, and the results obtained compare very favorably with those obtained by the electrodeposition of the metal. The quantities of nickel found agree within less than 0.1 mg. with those used with quantities of nickel ranging as high as 25 mg.

Ishimaru<sup>178</sup> has proposed a different titrimetric method in which nickel is precipitated with dimethylglyoxime, and the resulting precipitate decomposed with a warm solution of potassium dichromate that has been acidified with sulfuric acid. One ml. of 0.1 N potassium dichromate is equivalent to 0.000240 g. of nickel. In this procedure a known excess of the standard potassium dichromate-sulfuric acid solution is used for the decomposition; and then a known

volume of standard ferrous sulfate solution is added and the excess ferrous sulfate determined with standard potassium permanganate.

**Semi-quantitative determination of nickel by means of a spot test.** By carrying out spot tests upon reaction fields of unit surface area, and carrying out the tests so that the colored reaction product is uniformly distributed over the entire surface, it is possible to make a colorimetric estimation of the quantities of the reacting substances. Yagoda<sup>179,258</sup> has used this principal for the semi-quantitative determination of a number of metals using organic reagents for color reactions. A water repellent, such as paraffin, is used for the limitation of the area over which the reaction can take place, and the colored areas once formed are protected from the disturbing effects of atmospheric gases by impregnating with paraffin. Nickel can be approximately determined by this method.

**Detection and determination of cobalt.** Ammoniacal solutions containing cobalt salts react with dimethylglyoxime to form soluble brown compounds. Tschugaeff<sup>180</sup> prepared and studied a number of cobalt compounds containing dimethylglyoxime and ammonia or pyridine.<sup>181,182</sup> Braley and Hobart<sup>182</sup> were the first to use the reaction between cobalt and dimethylglyoxime for the detection and colorimetric determination of cobalt. The brown color is stable in an acetic acid solution, and 0.0005 mg. of cobalt per ml. gives a deep coloration. Considerable quantities of iron and copper obscure the color. This reaction can be made fairly satisfactory as a colorimetric method for cobalt if the acidity of the solution is controlled by the addition of sodium acetate, although a large excess of dimethylglyoxime decreases the accuracy of the procedure. Nickel, if present, is precipitated with dimethylglyoxime and removed by filtration before observing the color of the cobalt solution. The following procedure, which can be used for the detection or determination of cobalt, is taken from the work of Braley and Hobart:

**Procedure.** Slightly acidify the solution to be analyzed and add a 10 per cent solution of sodium acetate until the mixture is practically neutral. Heat to boiling and add an excess of a 1 per cent alcoholic solution of dimethylglyoxime. If nickel is present, filter, and allow the filtrate to cool slowly. If nickel is absent, omit the filtration. When the solution is cold, compare with standard solutions containing known quantities of cobalt and similarly treated.

The accuracy of this method is within 5-10 per cent.

The reaction between cobalt and dimethylglyoxime is far more sensitive when carried out in the presence of certain amines, particularly aromatic amines. Among the various amines which have been tried, benzidine has proved very satisfactory. A cobalt solution treated separately with a dilute alcoholic solution of benzidine or with an alcoholic solution of dimethylglyoxime does not become colored, but if these two reagents are added together, a beautiful orange-red color appears. Chiarottino<sup>183</sup> used this reaction as a sensitive test for cobalt. As the reagent he employed a solution prepared by dissolving 0.5 g. of benzidine and 0.25 g. of dimethylglyoxime in 100 ml. of 95 per cent ethyl alcohol. The

following procedure, based upon the Chiarottino reaction, has been proposed by Scott:<sup>68</sup>

**Procedure.** Dissolve the precipitate of nickel and cobalt sulfides, which is obtained in the analysis of Group III, in hydrochloric acid to which a little nitric acid has been added. Filter the mixture and evaporate the filtrate almost to dryness. Dissolve the residue in a few ml. of water containing 1 ml. of dilute acetic acid, and to this solution add 1 g. of solid sodium acetate, 0.5 ml. of a 0.5 per cent solution of benzidine in alcohol, and then an excess of a 1 per cent alcoholic solution of dimethylglyoxime. If nickel is present, as shown by the formation of characteristic red precipitate, filter the solution, and observe the color of the filtrate. In the absence of nickel, omit the filtration. If cobalt is absent, the filtrate will be colorless or yellow, but if cobalt is present the filtrate will have a red coloration. If the results of the test are doubtful, due to the low concentration of cobalt, add solid sodium acetate to intensify the color and allow mixture to stand for several hours. By this reaction, as little as 0.01 mg. of cobalt can be detected.

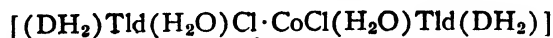
Chromium and copper interfere with this reaction by giving precipitates under the conditions of the test. The test is particularly well suited to the detection of cobalt in the usual scheme of qualitative analysis.

In a critical study of the reaction of Chiarottino, Spacu and Macarovici<sup>184</sup> claim that the reaction is much more sensitive than originally claimed, and they have found that it is still more sensitive if benzidine is replaced by tolidine. They have reported that the method can be used for detecting as little as 0.25γ of cobalt per ml. of solution. They recommend a 1 per cent alcoholic solution of dimethylglyoxime and a 1 per cent alcoholic solution of either benzidine or tolidine. The following method is used for the colorimetric determination of cobalt:

**Procedure.** Accurately measure 10 or 15 ml. of solution to be analyzed, and 10 or 15 ml. of a standard cobalt solution (which should be a little more concentrated than that of the unknown) into comparison tubes; and to each of the tubes add, from a small pipet, 0.5 ml. of 1 per cent alcoholic solution of dimethylglyoxime and mix well. Then add 0.2 ml. of a 1 per cent benzidine or tolidine solution. Mix well, and allow the mixture to stand for 15 minutes and compare in a colorimeter.

The greatest error observed in 26 determinations was about 0.9 per cent for 0.1 to 2.0 mg. of cobalt.

According to Spacu and Macarovici, the composition of the red compounds with dimethylglyoxime and benzidine or tolidine are given by the following formulas:



DH<sub>2</sub> = Dimethylglyoxime

Bzd = Benzidine

Tld = Tolidine

Brau<sup>185</sup> has replaced benzidine with a number of amines, and reports that dianisidine, tolidine and 2,7-diaminobenzofuran or 2,7-diaminofluorene may be used satisfactorily.

Another test for cobalt using dimethylglyoxime has been proposed by Matsui<sup>12</sup> and others.<sup>11,186,187</sup> Cobalt is first converted to the cobalt dimethylglyoxime compound, which is freed from nickel and iron, and then treated with a little ammonium polysulfide. A dark red color is formed in this reaction. If a mixture of nickel and cobalt is treated with dimethylglyoxime in the usual manner, and the nickel precipitate removed by filtration, the cobalt in the filtrate may be detected by adding a drop or two of ammonium polysulfide. A trace of cobalt is sufficient to give a red coloration.<sup>11</sup>

According to Malatesta,<sup>270</sup> the compound formed in this reaction corresponds to the formula  $[\text{Co}^{\text{III}}(\text{DH})_2\text{S}_n]\text{H}$ , where DH represents  $\text{CH}_3-\text{C}(=\text{NOH})-\text{C}(=\text{NO})-\text{CH}_3$ , and  $n$  may have a value of 3 to 5. The properties of this compound indicate that it is a polymer, linked presumably by S<sub>3</sub>, S<sub>4</sub> or S<sub>8</sub> bridges. It is an acid and capable of forming alkali salts.

Feigl and Tustanowska<sup>186</sup> have suggested the following procedure for detecting cobalt in the presence of nickel.

**Procedure.** Add sodium acetate to the nickel-cobalt solution to reduce the acidity, and then treat with an excess of dimethylglyoxime. Filter off the nickel precipitate and add a little dilute sodium sulfide solution to the filtrate. With cobalt, a violet coloration appears, and its intensity is proportional to the cobalt content of the solution. The test can be made more sensitive by shaking with a little amyl alcohol, in which a deep-violet to clear wine-red color appears. In this way 1 part of cobalt in 830,000 parts of solution can be detected.

The reaction of cobalt with dimethylglyoxime and a sulfide or polysulfide can be made considerably more sensitive by oxidizing cobalt to the trivalent state by means of hydrogen peroxide. The following procedure is taken from the work of Nilssen and Paulsen:<sup>187</sup>

**Procedure.** Make the solution to be tested alkaline with ammonium hydroxide, and add an excess of dimethylglyoxime (dimethylglyoxime may be added as the solid). Filter, if necessary, and treat with a few drops of hydrogen peroxide and heat to boiling. Add two drops of a solution of sodium polysulfide prepared by boiling sodium sulfide with 3-5 moles of sulfur. A clear blue color shows the presence of cobalt. With very small concentrations of cobalt, the solution may appear greenish in color.

The authors claim for this reaction a sensitivity of at least 1 part in 5,000,000. None of the common ions interfere with this test.

Recently Rossi and Coronato<sup>188,262</sup> have suggested that cobalt can be determined by means of the purple color which is formed when dimethylglyoxime,



together with a reducing agent such as sodium stannite, is added to a solution of a cobaltous salt.

**Detection of palladium.** Dimethylglyoxime reacts with solutions of palladium salts to give a yellow precipitate of palladium dimethylglyoxime. This compound is insoluble in dilute mineral acids. This reaction was first observed by Tschugaeff,<sup>189</sup> and was later used by Wunder and Thüringer<sup>190</sup> for the separation and determination of palladium. Palladium is quantitatively precipitated by dimethylglyoxime from solutions of dilute mineral acids, and the palladium compound appears to be completely insoluble in water. It dissolves readily, however, in ammonia and cyanide solutions. The palladium compound has the composition of  $\text{Pd}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$ , and undoubtedly has the same structure as that of the corresponding nickel compound.

Since palladium is precipitated by dimethylglyoxime from dilute acid solutions, and nickel is precipitated only from weakly acid or ammoniacal solutions, palladium may be detected by means of dimethylglyoxime without serious interference from other ions. Platinum is partially precipitated by the reagent, and gold is reduced to the metal; hence, these ions are likely to interfere with the palladium test. The following procedure may be used for the detection of palladium:

**Procedure.** Acidify the solution to be tested with a few drops of hydrochloric or sulfuric acid, and then add a few ml. of an alcoholic solution of dimethylglyoxime. Warm gently to precipitate palladium and to coagulate the precipitate. A bright yellow precipitate forms if palladium is present. If the precipitate is dirty yellow in color, gold or platinum is very likely present along with palladium.

Korenman and Kaplanskii<sup>191</sup> have proposed a procedure for detecting palladium by using a flotation method. The precipitate formed when dimethylglyoxime is added to an acid solution of a palladium salt and shaken with a water-ether mixture collects at the interface of the two liquids. This method is particularly useful in testing colored or pigmented solutions. The limiting concentration for detecting palladium without the use of a flotation method is approximately 1:150,000, while by using a flotation method the sensitivity is increased to 1:300,000. The presence of cadmium, nickel, copper, silver and bismuth have no effect upon this reaction.

Korenman<sup>192</sup> suggests the following microchemical reaction for palladium:

**Procedure.** Place a drop of the solution to be tested on a glass slide and evaporate to dryness by gentle warming, and then add a drop of a saturated solution of dimethylglyoxime in 2.5 per cent acetic acid in 50 per cent ethyl alcohol. Yellow needles appear in the presence of not less than 5 p.p.m. of palladium.

Gold interferes when present in considerable excess but other cations do not interfere.

Whitmore and Schneider<sup>193</sup> have studied the use of dimethylglyoxime as a

microchemical reagent for palladium and the platinum metals. Table 34 is taken from the work of Whitmore and Schneider. In these tests a solid fragment of the reagent was added to one per cent solutions of the platinum metal salts.

TABLE 34.—MICROCHEMICAL REACTIONS OF DIMETHYLGLYOXIME

Test Material	Description
PdCl <sub>2</sub>	An entangled mesh of very fine, long slender needles develops around the test particle and radiates from it into the drop. Crystals are yellow.
AuCl <sub>3</sub>	A very fine granular precipitate develops gradually around the reagent particle. Under higher magnification this precipitate is shown to be composed of a great number of small prisms. The other metals do not react with this reagent.

Feigl<sup>194</sup> has used an interesting spot reaction for the detection of small quantities of palladium: If a drop of a neutral solution of a palladium salt is placed upon paper which has been impregnated with nickel dimethylglyoxime, the red nickel salt is converted into the yellow palladium salt of dimethylglyoxime. Consequently, if considerable quantities of palladium are present, a yellow spot appears on the background of the red paper. Now if this paper is immersed in a dilute mineral acid, the nickel salt dissolves immediately, while the palladium salt, which is acid-resistant, remains unchanged. By this treatment the red paper is decolorized except the area which was spotted with the solution of the palladium salt. When very dilute solutions of palladium are used, however, entirely different results are obtained. No yellow spot is visible on the reagent paper, but when the paper is immersed in a dilute acid solution an intense red spot remains while the rest of the paper is decolorized. The following explanation has been offered for this phenomena: the nickel dimethylglyoxime within the capillaries of the paper reacts first with the palladium ions with the result that the surface of the nickel precipitate is covered with a layer of palladium dimethylglyoxime, and this layer prevents or retards the further penetration of the palladium solution. If the palladium solution is sufficiently dilute, the nickel dimethylglyoxime is covered only superficially, and the unchanged material lying beneath is protected from the action of the mineral acid. Hence, upon treating the paper with dilute acid, the nickel dimethylglyoxime which is not protected by the layer of palladium dimethylglyoxime is decolorized, while that covered by the thin coating of the palladium compound remains red. The protective action of solutions of palladium salts is observed even in the presence of extremely minute quantities of palladium. The remarkable protective action of minute quantities of the palladium compound is probably due to the fact that the palladium and the nickel salts of dimethylglyoxime are isomorphous, and mixed crystals are formed on the surface of the nickel dimethylglyoxime.

The following procedure for detecting palladium by this method is described by Feigl:<sup>194</sup>

**Reagent.** Immerse a strip of filter paper in a 1 per cent alcoholic solution of dimethylglyoxime and dry in current of warm air. Then place the strip of paper in a 2 N ammoniacal solution of nickel nitrate. The paper is then washed with water and alcohol and dried in a current of warm air. This reagent paper will keep for several weeks. On standing, however, the nickel dimethylglyoxime slowly crystallizes, and a part of it may fall from the paper, and in this way decrease the activity of the reagent.

**Procedure.** Place a drop of the solution to be tested, which contains not more than 0.01 per cent palladium chloride, on the reagent paper and when the drop is completely absorbed, place the paper in a solution of dilute hydrochloric acid. The red paper turns white immediately, except for the spotted area, which remains red if palladium is present. The paper is then soaked in water to wash out the acid.

By means of this reaction as little as 0.05 $\gamma$  of palladium in one drop can be detected. According to Feigl<sup>195</sup> this test is specific, since under the conditions outlined no other metals react or decrease the sensitivity of the test.

Miller and Lowe<sup>196</sup> have used dimethylglyoxime for the detection of palladium in a systematic scheme of analysis.

**Determination of palladium.** Since palladium is quantitatively precipitated by dimethylglyoxime from solutions of dilute mineral acids, many investigators have used this reagent in procedures for the determination of palladium.<sup>88,190,197,198</sup> The palladium dimethylglyoxime precipitate is so insoluble that no special precautions are necessary to insure completeness of precipitation as long as only dilute hydrochloric or sulfuric acid is present in the solution from which precipitation occurs. Wunder and Thüringer<sup>199</sup> have studied the solubility of palladium dimethylglyoxime in various media and have reported their results in Table 35.

TABLE 35.—SOLUBILITY OF PALLADIUM DIMETHYLGLYOXIME

Medium	Solubility
Water .....	0.002 per cent
2 Per cent hydrochloric acid .....	0.0013 per cent
20 Per cent acetic acid .....	0.0021 per cent
50 Per cent alcohol .....	0.0018 per cent

If nitrates are present in the solution, precipitation of palladium appears to be incomplete.

The precipitate, which contains 31.67 per cent of palladium, may be dried at 115° C. and weighed as such. Tashiro<sup>200</sup> has studied the drying temperature of the precipitate by means of the thermobalance, and reports that it may be safely dried over a temperature range of from 100 to 120° C., but that above 120° C. oxidation introduces some error. This method of handling the precipitate is entirely satisfactory and by far the most convenient. An

alternate procedure, however, has been proposed in which the precipitate of palladium dimethylglyoxime is wrapped in an extra layer of filter paper, carefully charred, the filter paper burned away, and palladium then reduced to the metal by igniting in hydrogen, and finally the metal is ignited and cooled in an atmosphere of carbon dioxide. Since palladium absorbs a rather large quantity of hydrogen, it is difficult to bring the precipitate of the metal to constant weight. This difficulty is eliminated by igniting the metal in an inert gas. Strong ignition in air is sufficient to decompose all oxides of palladium without the necessity of using hydrogen, but in this case the metal tarnishes after it cools unless an inert gas is used to protect it. The error introduced by the slight tarnishing of the metal amounts to only 0.1 mg. with quantities of palladium weighing 100 mg.<sup>201</sup>

Many procedures have been studied for the analysis of mixtures of the platinum metals which may contain gold and other metals with which they frequently are mixed or alloyed. Many of these procedures include the use of dimethylglyoxime for the determination of palladium. According to some reports<sup>149,202-205</sup> it is possible to precipitate palladium from slightly acid chloride solutions by means of dimethylglyoxime without contamination of the precipitate by platinum or the platinum metals, but according to more recent studies<sup>206-210</sup> it appears that platinum may also be precipitated along with the palladium.

Thompson, Beamish, and Scott<sup>207</sup> have more recently studied the precipitation of palladium in the presence of platinum and report that high results are often obtained if platinum is present.

Holzer,<sup>210</sup> however, reports that the separation is satisfactory if a few drops of perhydrol is added to the solution before the introduction of dimethylglyoxime. He claims that good results are obtained in determining 1-4 mg. of palladium in the presence of 3-6 mg. of platinum.

Gilchrist and Wichers<sup>201,211,212</sup> have developed a satisfactory procedure for determining palladium in a scheme for the analysis of platinum metals. They have found that palladium may be satisfactorily determined in the presence of rhodium and iridium, and that a solution containing only palladium, rhodium, and iridium can easily be prepared. According to their procedure, palladium, rhodium and iridium are separated from platinum, which may interfere with the palladium determination, by precipitation of these three metals as the hydrated oxides. The following procedure is recommended:

**Procedure.** *Separation of palladium, rhodium and iridium from platinum:* Heat the solution containing platinum, rhodium, iridium and palladium to boiling, and add 20 ml. of a filtered 10 per cent solution of sodium bromate. Carefully add a filtered 10 per cent solution of sodium bicarbonate until the dark green solution shows evidence of the formation of a permanent precipitate. Test the acidity of the hot solution from time to time by allowing a drop of 0.01 per cent bromocresol purple indicator solution to run down a stirring rod into a drop of the solution which adheres to it after removal from the solution which is being neutralized. A sufficient quantity of the bicarbonate is indicated when the color of the indicator changes from yellow to blue. At this point add an additional 10 ml. of the bromate reagent and boil for 5 minutes. Continue to

add the sodium bicarbonate solution dropwise until a faint pink color is obtained in a test drop with 0.01 per cent cresol red. Again add 10 ml. of the sodium bromate solution and boil for 15 minutes. Filter the mixture, using suction, through a porcelain filter crucible having solid walls and a porous bottom. Transfer the precipitate to the crucible and wash with a hot 1 per cent solution of sodium chloride, the acidity of which has been carefully adjusted to pH 6-7.

Place the crucible with the precipitate and the stirring rod in the beaker originally used for the precipitation, cover with a watch glass, and then add 10-20 ml. of hydrochloric acid, pouring most of the acid into the crucible. Now place the beaker and its contents on a steam bath and heat for a short time. Remove the crucible and wash thoroughly with water, and then place in a 250 ml. beaker and pour into the crucible 5 ml. of hydrochloric acid. Cover the beaker with a watch glass and heat on a steam bath. Repeat the treatment with fresh acid in order to remove completely the precipitated oxides. Finally combine the leachings with the main portion of the dissolved precipitate. Add 2 g. of sodium chloride, and evaporate the solution to dryness on a steam bath. Add 2 ml. of hydrochloric acid, dilute the solution to 300 ml. with water, and repeat the precipitation of the hydrated oxides according to the above procedure. The second precipitation is necessary to remove platinum completely. Again dissolve the precipitated oxides in hydrochloric acid according to the above procedure, and thus prepare a solution of the chlorides of palladium, rhodium and iridium. The sodium bromate used in precipitating the oxides interferes with the palladium determination and must be removed by treatment with hydrochloric acid.

*Determination of palladium:* Make the solution containing palladium, iridium and rhodium (or a solution of palladium chloride, if no interfering elements are present), weakly acid with hydrochloric or sulfuric acid, and dilute to about 400 ml. Precipitate palladium by adding a 1 per cent alcoholic solution of dimethylglyoxime. For this precipitation, add 2.2 ml. of the reagent for each 10 mg. of palladium present, and then add an excess of about 10 per cent to insure complete precipitation. Allow the mixture to stand for 1 hour and filter.

It is often necessary to reprecipitate palladium to insure complete removal of interfering substances. This is accomplished as follows: Filter on paper, wash the precipitate with 1:99 hydrochloric acid, and then with hot water, and then transfer the washed filter and precipitate to an Erlenmeyer flask. Close the flask with a short-stemmed funnel and decompose the mixture with a solution of sulfuric and nitric acid. Heat the mixture until fumes of sulfuric acid are evolved, and then dilute somewhat with water and filter. Palladium is reprecipitated in the diluted solution with dimethylglyoxime.

If palladium is to be weighed as palladium dimethylglyoxime filter the precipitate on a porcelain or glass filter crucible with suction. Wash the precipitate with 1:99 hydrochloric acid, and then with hot water, and dry at 110° C. for 1 hour. Calculate the quantity of palladium in the precipitate by using the factor 0.3167.

If the palladium is to be weighed as the metal, filter the precipitate on paper, and wash as described above. Thoroughly cleanse the inner walls of the beaker in which the precipitation was carried out, and also the stirring rod with a small piece of filter paper. Wrap the filter and the precipitate, along with the piece of filter paper used to cleanse the beaker and stirring rod, in a second sheet of filter paper and place them in a porcelain crucible. Dry and ignite carefully in air with only sufficient heat being supplied to keep the paper smoking gently. Ignite the charred residue strongly in air, and then in hydrogen, and finally ignite the metallic palladium in carbon dioxide for two minutes and cool in carbon dioxide. Weigh the residue as metallic palladium.

Beamish and Russel<sup>213</sup> state that iridium, osmium, rhodium and ruthenium are not precipitated when palladium is precipitated with dimethylglyoxime.

Zschiegner<sup>214</sup> has studied the determination of palladium in alloys and has developed the following procedure:

**Procedure.** Dissolve 2 g. of the alloy in aqua regia and evaporate the resulting solution to dryness. Dissolve the residue in 100 ml. of water and heat slowly to boiling. Add 5 g. of sodium nitrite and stir until the chlorides are all dissolved. Then dilute to 250 ml. and add an additional 5 g. of sodium nitrite. Heat to 80° C. for one hour, being careful not to exceed 80° C. Cool, neutralize with sodium carbonate, and add 0.2 ml. of N sodium carbonate in excess, using phenolphthalein as the indicator. Filter off the gold, silver and base metals, and precipitate palladium with dimethylglyoxime. Filter and weigh as palladium dimethylglyoxime.

Palladium may be determined satisfactorily in gold-palladium-silver alloys by precipitating palladium with dimethylglyoxime.<sup>215,216</sup>

**Separation of nickel from palladium.** Nickel and palladium may be separated by a method based on the fact that palladium is quantitatively precipitated in a cold mineral acid solution, while nickel is precipitated only in slightly acid or alkaline solutions.<sup>217,218</sup> The following procedure may be used:

**Procedure.** Slightly acidify with hydrochloric acid a solution containing nickel and palladium, and add an excess of a 1 per cent solution of dimethylglyoxime in a 2 per cent solution of hydrochloric acid. Digest on a water-bath for 30 minutes and filter the warm solution. Wash with boiling water, dry, ignite and weigh as metallic palladium.

Nickel may be determined in the filtrate by making slightly alkaline with ammonium hydroxide. Under these conditions the nickel salt is completely precipitated and may be filtered, washed with boiling water, and then with alcohol, and finally dried at 100° C. at constant weight. The factor for nickel is 0.2031, and for palladium 0.3161.

Golbraikh<sup>206</sup> has used dimethylglyoxime for the determination of small amounts of palladium in the presence of large quantities of nickel.

**Separation of palladium from copper and iron.** Wunder and Thüringer<sup>190</sup> have used dimethylglyoxime for the separation of palladium from copper and iron.

**Procedure.** Make the solution containing the palladium salt acid with hydrochloric acid, and dilute to 150 ml. with water. Precipitate palladium by means of a 1 per cent solution of dimethylglyoxime in 2 per cent hydrochloric acid. Allow to stand for 30 minutes on a water bath, filter, wash the precipitate, dry, ignite, and weigh the residue as metallic palladium.

If the solution to be analyzed contains copper and iron, a large excess of the dimethylglyoxime solution should be used, as some of the iron may be reduced if present as ferric chloride.

**Separation of palladium and tin.** Gutbier and Fellner<sup>210</sup> recommend the following procedure for separating palladium and tin:

**Procedure.** Dissolve the palladium which contains tin in aqua regia, and expel the free chlorine by heating. Dilute the resulting solution to at least 150 ml. and heat on a water-bath, and then add a 1 per cent alcoholic or hydrochloric acid solution of dimethylglyoxime with stirring until precipitation is complete. Heat the mixture until the precipitate has settled and then cool to room temperature. Filter and wash with 1-2 per cent hydrochloric acid, ash, and burn in a Rose crucible, and finally ignite in hydrogen and weigh as palladium.

**Determination of gold.** Gold is quantitatively precipitated as the metal when a solution of a gold salt is treated with dimethylglyoxime. This reaction has been made the basis for a satisfactory method for determining gold.<sup>88,207</sup> The following procedure is recommended by Thompson, Beamish and Scott:<sup>207</sup>

**Procedure.** Dilute the solution containing 10-25 mg. of gold to 50 ml., and acidify with about 0.5 ml. of concentrated hydrochloric acid, and then add 100 mg. of dimethylglyoxime in a 1 per cent alcoholic solution. At this point a yellow precipitate begins to form. Boil for 30 minutes, and filter the precipitated gold through a filter crucible. Wash well with water and weigh as metallic gold.

TABLE 36.

Determination	Weight of Gold Taken	Weight of Gold Found
No. 1	24.92 mg.	24.90 mg.
No. 2	24.92 mg.	24.87 mg.
No. 3	10.01 mg.	9.99 mg.
No. 4	10.01 mg.	9.99 mg.

Results shown in Table 36, which are taken from the work of Thompson, Scott and Beamish,<sup>207</sup> confirm the authors' claim that the determination of gold by this method is satisfactory.

Whitemore and Schneider<sup>198</sup> have investigated the use of dimethylglyoxime as a microchemical reagent for gold, and show that this reagent can be used to some advantage. When a solid fragment of the reagent is added to a drop of a 1.0 per cent aqueous solution of gold chloride, a very fine granular precipitate forms around the particle of the reagent. Under high magnification this precipitate is seen to consist of a great number of small prisms.

Dimethylglyoxime may be used to separate gold and palladium from the other metals of the platinum group, except platinum, as a preliminary to the determination of gold and palladium. In a hot solution containing hydrochloric acid, dimethylglyoxime precipitates gold as the metal and palladium as yellow palladium dimethylglyoxime complex. The following procedure has been proposed by Wunder and Thüringer:<sup>199</sup>

**Procedure.** Make the solution containing gold, palladium and the metals of the platinum group (except platinum) slightly acid with hydrochloric acid, and add an excess of a hot aqueous solution of dimethylglyoxime. Heat for some time, cool, filter through hardened paper, and wash with a 1 per cent solution of hydrochloric acid. Dry and ignite carefully, finally heating with a blast lamp. Dissolve the residual metals in aqua regia, and evaporate to dryness repeatedly with hydrochloric acid. Dissolve the residue in warm water and add 1-2 g. of ammonium oxalate. Heat at a temperature not exceeding 60° C. for several hours. Add 10-15 ml. of dilute sulfuric acid and filter off the precipitated gold on a hardened paper. Wash with dilute sulfuric acid, and then with 1 per cent hydrochloric acid. Dry, ignite, and weigh as metallic gold.

Neutralize the excess acid in the filtrate with ammonium hydroxide and add dimethylglyoxime to the boiling solution. Cool, filter, and wash with warm water. Ash carefully, reduce in hydrogen, cool in carbon dioxide, and finally weigh as metallic palladium.

**Precipitation of platinum.** When sodium formate is added to a slightly acid solution of chloroplatinic acid containing an alcoholic solution of dimethylglyoxime, platinum dimethylglyoxime forms as a fine, blue crystalline precipitate, having a characteristic metallic bronze luster. According to Cooper,<sup>206</sup> precipitation is quantitative, but the precipitate cannot be ignited to the metal without loss, although when dried at 100° C. and weighed as  $C_8H_{14}O_4N_4Pt$  satisfactory results can be obtained. Wunder and Thüringer<sup>208</sup> and Thompson, Beamish and Scott,<sup>207</sup> however, have used this method and report unsatisfactory results. Thompson and co-workers claim that dimethylglyoxime may be used as a reliable test for platinum, although this test is not sensitive. In a recent investigation, these authors report that the precipitation of platinum with dimethylglyoxime is not complete, but that this reaction may be very useful in certain separations involving platinum. Although Cooper<sup>206</sup> recommends the use of sodium formate for reducing platinum, Thompson does not find that this hastens or causes a more complete precipitation of the metal.

**Detection and determination of ferrous iron. Detection of iron.** Tschugaeff<sup>189</sup> first observed that ferrous iron reacts with the  $\alpha$ -orthodioximes in the presence of ammonia, pyridine or aliphatic amines to form soluble red or violet



compounds. According to Tschugaeff these compounds correspond to the general composition  $\text{Fe}(\text{DH})_2\text{A}_2$ , where  $\text{DH}_2$  represents one molecule of dioxime and A a molecule of ammonia, pyridine or amine. Little attention was apparently paid to the work of Tschugaeff, since no effort appears to have been made to apply this reaction to the detection of iron. Slawik<sup>220</sup> and others observed the appearance of a red color in various procedures for the analysis of nickel, and many errors appear to have been made by not recognizing the red color as being caused by ferrous iron.<sup>10,221,222</sup> Slawik<sup>220</sup> was the first to apply this reaction as an extremely sensitive test for iron. Dimethylglyoxime reacts with ferrous iron to give a red color similar to that formed with rosolic acid and alkalies, and this color slowly disappears as the ferrous iron is oxidized to the ferric state by atmospheric oxygen. Stannous chloride or zinc, however, may be used as reducing agents to restore this color.<sup>223</sup>

In the absence of ammonia, pyridine or amine, dimethylglyoxime reacts with ferrous iron to produce only a weak yellow color. Ferric iron does not yield the deep red color which is characteristic of ferrous iron, but can be prevented from interfering with the ferrous test by the addition of a citrate or tartrate, which prevents the precipitation of ferrous hydroxide on the addition of ammonia or amine.

**Procedure.** Add a few drops of a 1 per cent alcoholic solution of dimethylglyoxime to the solution to be tested, and add a slight excess of ammonia. Heat the solution for a few minutes and observe the color. A rose-red color indicates the presence of ferrous iron. This color may be more easily observed by holding the solution against a white background. A blank should be run on the reagent. If ferric iron is also present, and almost invariably it is, add tartaric acid before making the solution ammoniacal in order to prevent the precipitation of ferric hydroxide.

The above reaction, which is used only for detecting ferrous iron, may be modified as a general reaction for iron. Ferric iron is first reduced to ferrous iron by the addition of hydrazine sulfate, and then the test is applied as above. The sensitivity of this reaction as a test for iron is very great. It is reported that as little as 0.00005 mg. of iron, corresponding to 1 part in 20,000,000 may be detected by this reaction.

Because of rapid atmospheric oxidation, minute quantities of ferrous iron in the presence of ferric iron may escape detection. By means of a test paper impregnated with dimethylglyoxime, it is possible to detect as little as 1 part of ferrous iron in the presence of 200,000 parts of ferric salt by means of the above reaction.<sup>258</sup> Tartaric acid is used to prevent precipitation of ferric hydroxide when the mixture is made alkaline.

According to Vaubel,<sup>221</sup> the red color can be obtained with iron salts without the use of a hydrazine salt as a reagent. Ammonium sulfide intensifies the color greatly.

**Procedure.** To 20 ml. of a 1 per cent alcoholic solution of dimethylglyoxime add 20 ml. of the iron solution to be analyzed and dilute to 50 ml. Then

add 10 drops of ammonium sulfide solution and 10 drops of ammonium hydroxide and dilute the mixture to 100 ml.

Ferrous salts when treated with ammonia and dimethylglyoxime give an intense deep red color, while ferric salts similarly treated give a brownish-yellow to yellowish-red coloration. Ferric salts, however, in the presence of ammonia and ammonium sulfide give an intense deep-red color.

Ferrous iron in a neutral aqueous solution gives a characteristic microcrystalline precipitate with dimethylglyoxime and pyridine vapor.<sup>297,298</sup> In this way 0.1 $\gamma$  of iron can be detected.

**Determination of iron.** Tschugaeff and Orelkin<sup>224</sup> have applied the reaction between ferrous iron and dimethylglyoxime to the colorimetric determination of iron.

**Procedure.** Add 1 g. of hydrazine sulfate and 5 ml. of a saturated alcoholic solution of dimethylglyoxime to 50-70 ml. of the solution to be analyzed and heat to boiling. Then add 10 ml. of concentrated ammonium hydroxide and continue to boil for 30 seconds. Cool the solution quickly under running water and dilute to 100 ml. Immediately transfer the solution to a colorimeter and compare with a standard solution simultaneously and similarly prepared.

By means of this reaction iron can be determined with an accuracy of 1-2 per cent if the iron concentration is 0.001-0.00005 N. The alkali and alkaline earth metals and magnesium have no effect upon this determination, although large amounts of zinc and aluminum interfere.

Von Stem<sup>205</sup> has used this method for the rapid determination of iron in plant control of samples to be run for iron.

Nakaseko<sup>225</sup> has used a similar method for the microchemical determination of iron, and has employed hydrogen sulfide as the reducing agent. According to his investigation, the tint and depth of color produced on mixing solutions containing iron, hydrogen sulfide, ammonia, and dimethylglyoxime vary, depending upon the order in which they are mixed, but that they are constant under specific conditions. According to the method of Nakaseko, the test solution is first treated with a freshly prepared, saturated solution of hydrogen sulfide to reduce ferric salts, and the mixture is then treated with a 1 per cent alcoholic solution of dimethylglyoxime, and finally with ammonia. This method and the thiocyanate method are about equally sensitive.

**Detection and determination of copper.** Certain oxidizing agents, when added to very dilute, slightly alkaline solutions of cupric salts containing dimethylglyoxime, produce an intense reddish-violet color resembling that of the permanganate ion. This reaction was first observed by Clarke and Jones<sup>226,265</sup> and was later studied and applied as an analytical reaction by Hurd and Chambers,<sup>227</sup> Kolthoff,<sup>228</sup> and Goethals.<sup>229</sup> The color produced by sodium hypochlorite or bromine water is very fugitive, partly due to the fact that the color is sensitive to acids and to excess alkalis, and also to the difficulties encountered in adjusting the pH when using these oxidizing agents. Ammonium persulfate appears to be one of the more satisfactory oxidizing substances. This reagent causes the

appearance of a weak reddish-color, but when a little silver nitrate is added, an intense permanganate color develops immediately. This is particularly true when pyridine is used as a means of obtaining the proper alkalinity. Potassium periodate is also a satisfactory oxidizing agent.

The nature of this reaction has not been definitely established. It has been observed, however, that in the presence of a fairly large excess of periodate, the red color formed in the reaction with copper fades rather rapidly, but that it may be restored by the addition of more dimethylglyoxime. From this it may be inferred that dimethylglyoxime is oxidized by the periodate to form an unknown product which yields with copper a red colored compound; and this in turn is converted to a colorless compound by an excess of the oxidizing agent. The following procedure, which has been used both for the detection and colorimetric determination of copper, is the Hurd-Chambers modification of the original Clarke-Jones reaction.<sup>261</sup>

**Procedure.** Neutralize the solution to be tested, which must be free from chloride, and then make faintly acid by the addition of 2 ml. of 0.4 N of sulfuric acid. Place this solution in a 100 ml. Nessler tube, dilute to the mark, and add 1 g. of ammonium persulfate. Then add 1 ml. of a saturated alcoholic solution of dimethylglyoxime, 0.5 ml. of a 0.5 per cent solution of silver nitrate, and 2 ml. of 10 per cent aqueous pyridine and stir well.

To make this procedure quantitative place the same quantities of reagents in a similar Nessler tube and allow a standard solution of copper sulfate containing 0.1 mg. of copper per ml. to flow in until the color just matches that of the unknown solution. The color comparison should be made immediately, since the color shows some tendency to fade on standing.

As little as 0.01 mg. of copper yields a distinct violet-reddish color, and one part of copper in 10,000,000 parts of water can readily be detected. The above method, however, is not suitable for determining more than 0.1 mg. of copper. The intensity of the color produced in the above reaction depends upon various factors, and consequently for accurate results the directions should be carefully followed. For example, the intensity of the color depends upon the amount of pyridine used in making the solution alkaline, and exactly the quantity indicated must be added. The color reaches its maximum intensity in about 5 minutes when the amount of copper present is 0.030 mg.; and at higher concentrations of copper, the color reaches a maximum immediately and then begins to fade rapidly.<sup>261</sup> Callan and Henderson<sup>266,267</sup> have found that slight variations in the pH of the solution cause a change in the intensity of the color produced with copper and the reagent. If the concentration of sulfuric acid in the beginning of the procedure exceeds 0.008 N, the coloration produced is very faint and fugitive, and the addition of pyridine does not stabilize the color. A quantity of silver nitrate considerably in excess of the amount indicated in the procedure tends to cause a rapid fading of the color, and also appears to be responsible for formation of a yellow coloration which interferes with the color comparison. A material increase in the initial concentration of ammonium persulfate also causes rapid fading.

Chlorides must be absent from solution to be analyzed, since otherwise precipitation of silver chloride occurs, and this limits somewhat the applications of the copper test. Chlorides present in water may cause a turbidity due to the formation of silver chloride, but it has been recommended that this be discharged by the addition of an excess of pyridine. With this treatment, however, the color intensity for a given amount of copper is greatly reduced. If the chloride content of the solution exceeds 0.0005 mg. per ml., the method is not reliable, and should be used only when approximate values are required.

Small quantities of certain of the heavy metals cause yellow or brown colorations under the conditions of the test, but the reddish-violet color appears to be specific for copper. Iron may cause serious error if present in quantities exceeding 0.002 mg. per ml., and cobalt interferes when present in concentrations greater than 0.00002 mg. per ml. Sulfates and nitrates do not appear to affect this determination. Kolthoff<sup>228</sup> has proposed the following modification of the method of Hurd and Chambers.

**Procedure.** To 10 ml. of the solution to be tested add 1 ml. of a solution prepared by mixing 100 ml. of N sodium acetate and 7 ml. of N acetic acid, and then add 0.2-0.3 ml. of a 0.1 per cent solution of dimethylglyoxime and 1 ml. of a saturated solution of potassium periodate. Allow to stand for 3-5 minutes and observe the color. A violet-red color appears if copper is present. By means of this reaction as little as 0.1 mg. of copper can be detected in 1 liter of solution.

This procedure can be used for the detection of copper in water if only traces of zinc or lead are present. When the concentration of lead or zinc does not exceed 10 mg. per liter, there is little appreciable influence upon the color, but the color is somewhat weaker than in a blank solution prepared without these cations. With larger concentrations of these metals, the corresponding periodates may be precipitated and the sensitivity of the test materially decreased. Ferric iron also interferes with this reaction, although 1 mg. of copper in 1 liter of solution may be detected in the presence of 10 times as much iron. If 1 or 2 drops of 1 N disodium phosphate solution is added in making the test, 1 mg. of copper can be detected in 1 liter of solution in the presence of 20 times as much iron. Cadmium, manganese, and other cations interfere since they are precipitated upon the addition of the periodate.

**Miscellaneous reactions. Detection of bismuth.** Kubina and Plicta<sup>280,284</sup> observed that when a solution of the chloride or nitrate of bismuth is treated with dimethylglyoxime, and the hot solution is then made strongly alkaline with ammonia, an intense yellow, very voluminous precipitate is formed. A yellowish white precipitate, which appears to be a mixture of the basic salt and the yellow compound, is formed if the solution is only slightly ammoniacal. If precipitation is carried out in a cold solution, only the white basic salt is produced, but the yellow compound eventually forms on standing. Solutions of bismuth sulfate do not respond to this reaction, since only a white precipitate is formed, and this is not changed on heating. If a chloride or nitrate is added to the solution, however, and the solution heated, the yellow compound is quickly formed.

The yellow bismuth compound is decomposed by acetic acid with the formation of the basic salt, and ammonium sulfide converts it to bismuth sulfide. The formation of the yellow compound is prevented by the addition of tartrates; and this makes possible the detection of nickel in the presence of large quantities of bismuth by means of dimethylglyoxime.

Small quantities of bismuth cause the formation only of a yellow color on the addition of ammonia, and only after standing for some time does the yellow precipitate form. The reaction may be made more sensitive when dilute solutions are employed if the precipitate is collected on filter paper.

Arsenic, antimony, tin, cobalt, ferric iron, and manganese interfere with the bismuth test. Copper, which forms a dark brown soluble compound with dimethylglyoxime, does not interfere unless present in large quantities. It is necessary, however, in detecting bismuth in the presence of copper to dilute the solution before applying the test, and then to filter in order to observe the yellow precipitate of the bismuth compound.

Attempts to determine bismuth by precipitation with dimethylglyoxime have been unsuccessful because of the tendency of bismuth to form basic salts on dilution.

**Detection of vanadium.** In alkaline solutions, the vanadyl ion is oxidized to vanadate by ferric ions, while in an acid solution the reverse reaction takes place. Since the presence of ferrous iron in the solution can be detected by means of the red color which it yields in ammoniacal solutions with dimethylglyoxime, the above reaction serves as an indirect method for the detection of vanadium. The following procedure is suggested by Ephraim.<sup>281</sup>

**Procedure.** To 1 ml. of the solution to be tested, add 1 ml. of concentrated hydrochloric acid and evaporate rapidly to 0.4 ml. in a test tube. This causes a reduction of vanadic acid to the vanadyl ion ( $\text{VO}^{++}$ ). Immerse the tube in water until cool and add 1 drop of a freshly prepared 0.1 per cent solution of ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and 2 drops of 1 per cent alcoholic solution of dimethylglyoxime. Then make alkaline with ammonium hydroxide. If vanadium is present a red color due to the conversion of ferric to ferrous iron appears. To protect the reaction mixture from atmospheric oxidation, cover with a layer of petroleum ether.

By means of this reaction vanadium can be detected at a concentration of 1:400,000.

**Detection of cerium.** Ephraim's test for vanadium (see above), when suitably modified, can be applied to the detection of cerium. When solutions of ceric salts are boiled with hydrochloric acid, the ceric ion is reduced to the cerous state; and when this solution is treated with sodium or ammonium hydroxide, the cerous hydroxide which is formed reduces added ferric ions to the ferrous state, and the ferrous salts so formed react with dimethylglyoxime to yield a red color. The red color, however, is hidden by the precipitates which are formed in the reaction. To obtain a visible color test, proceed according to the method of Beck.<sup>282</sup>

**Procedure.** Fill a 4-cm. test tube approximately one-third full with a solution containing the cerous ion, and add an equal volume of 1 per cent alcoholic solution of dimethylglyoxime, 1-2 drops of 0.1 per cent ferric chloride solution, and then fill nearly to the top with water. Finally fill with ammonium hydroxide. Insert a tightly fitting stopper, and mix rapidly by inverting the test tube. All air must be excluded from the tube. A pink to deep-red color is obtained in the presence of cerium, although if only traces of cerium are present it is best to allow the tube to stand overnight. By means of this reaction as little as 1% of cerium can be detected.

Carbonates must be absent while making this test, since cerous carbonate is so stable that the red color of ferrous dimethylglyoxime is not formed. In this respect the reaction of cerium differs from that of vanadium.

**Detection of tin.** A procedure somewhat similar to those for vanadium and cerium may be used for the detection of tin. Ferric chloride is reduced by stannous chloride to the ferrous ion, and this in turn gives with dimethylglyoxime a red color in an alkaline solution. Ferric hydroxide is prevented from precipitating by adding citric or tartaric acid or a tartrate. Feigl<sup>233</sup> has used this reaction to detect tin in a systematic scheme of analysis. The sulfides of antimony and tin, obtained in the usual procedure, are dissolved in warm concentrated hydrochloric acid, and a portion of the resulting solution is treated with zinc to precipitate antimony and tin. Tin is redissolved with the aid of concentrated hydrochloric acid; and, after filtering, the resulting solution is poured into a hot dilute solution of ferric chloride. A little citric acid or sodium potassium tartrate is added, and the solution is made alkaline. A little 1 per cent alcoholic solution of dimethylglyoxime is then added. If tin is present, the red color of ferrous dimethylglyoxime appears.

**Compounds of dimethylglyoxime and rhodium.** Rhodium diaminedimethylglyoxime chloride,  $[\text{Rh}(\text{NH}_3)_2(\text{DH}_2)]\text{Cl} \cdot 5\text{H}_2\text{O}$ , is formed when  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  is heated with dimethylglyoxime, ammonium acetate and water at 150° C. ( $\text{DH}_2$  = dimethylglyoxime).<sup>234</sup>

This compound is not decomposed by dilute acids or alkalies, but it is decomposed on heating by concentrated sulfuric or nitric acids. The addition of sodium nitrate to the aqueous solution yields a precipitate of the nitrate; potassium iodide yields the corresponding iodide; sodium perchlorate, the perchlorate; and chloroplatinic acid, the chloroplatinate: Dichlorodimethylglyoxime-rhodic acid,  $[\text{RhCl}_2(\text{DH}_2)]\text{H}$ , is obtained as a heavy yellow, sandy precipitate by treating  $\text{Na}_2\text{RhCl}_6$  with dimethylglyoxime in a boiling aqueous solution.<sup>234</sup>

Chlororhodium bisdimethylglyoxime can be converted by treating with ammonium polysulfide into  $[\text{Rh}(\text{DH})_2\text{S}_6]\text{H}$ , which resembles the cobalt compound.<sup>234</sup>

**Determination of lead.** Lead is precipitated quantitatively with dimethylglyoxime as  $\text{Pb}_2(\text{C}_4\text{H}_8\text{N}_2\text{O}_2) \cdot \text{H}_2\text{O}$ . This reaction has been used by Ishibashi and Funahashi<sup>235</sup> for the gravimetric determination of lead. The solubility of the lead salt in water at 20° C. is equal to 1.60 g. of lead per liter,

but in a 0.25 per cent solution of ammonia it is only 0.65 mg. of lead per liter at 20° C.

**Detection of rhenium.** Rhenium may be detected in an acid solution in the presence of stannous chloride by means of a reaction with dimethylglyoxime. This reagent gives a yellow color which becomes green on heating. By means of this test, approximately 0.01 mg. of rhenium can be detected.<sup>236,262</sup> In a critical review of the methods used for detecting rhenium, Wenger and Duckert<sup>237</sup> have recommended dimethylglyoxime as one of the most satisfactory reagents which they examined.

**Detection of insoluble silver salts.** Feigl<sup>238</sup> has proposed an interesting procedure for detecting silver halides, cyanide, and thiocyanate. The insoluble silver salt dissolves in a solution of  $K_2Ni(CN)_4$ , which is prepared by dissolving nickel cyanide in potassium cyanide, with the formation of sufficient nickel to give a test with an alcoholic solution of dimethylglyoxime.

**Detection of oxidizing and reducing agents.** Ferrous iron in the presence of ammonium hydroxide yields a dark reddish complex with dimethylglyoxime. The color of the complex is discharged by such oxidizing agents as permanganates, hypochlorites, hypobromites, hypiodites, persulfates, iodates and ferricyanides. The color is restored by the addition of reducing agents such as cerous, stannous, vanadyl and thiosulfate ions, soluble sulfides or hyposulfites.

Charlot<sup>239</sup> has used these reactions as the basis for a very sensitive test for oxidizing and reducing agents. Oxidizing agents can be detected by means of the following procedure:

**Procedure.** Mix 1 drop of 0.1 N ferrous sulfate, 10 drops of 1 per cent alcoholic dimethylglyoxime, and a little ammonium hydroxide, and then dilute with water to 10 ml. To this solution add a little of the solution to be tested. The red color of the reagent is discharged in the presence of oxidizing agents.

A sensitive reagent for reducing substances is obtained by adding potassium ferricyanide solution to the red reagent used for detecting oxidizing substances until the color is just discharged: the red color reappears on the addition of reducing agents.

**The detection of a basic reaction in slightly soluble materials.** Feigl and da Silva<sup>240</sup> have used the following method for the detection of the basicity of slightly soluble materials:

**Reagent.** Prepare 3 reagents as follows:

(a) Add 100 ml. of 1 per cent alcoholic dimethylglyoxime to 50 ml. of 4 per cent nickel nitrate solution.

(b) Add 100 ml. of 1 per cent alcoholic benzoinoxime to 50 ml. of 4 per cent copper nitrate solution.

(c) Add 100 ml. of a 1 per cent alcoholic thionalide solution to 50 ml. of 4 per cent nickel nitrate solution.

Heat the above solutions for a short time on a water bath and filter. In this way three reagents are prepared containing nickel or copper ions, an excess of the organic reagent, and low concentration of the hydrogen ion, corresponding respectively to pH 1.9, 1.6, and 2.9. If the free acid is neutralized, the nickel or copper ions are precipitated as red nickel dimethylglyoxime, green copper benzoinoxime or dark brown nickel thionalide.

**Procedure.** To test insoluble materials for basic reaction, place 0.5-1.0 mg. of a slightly soluble material on a white spot plate, and add 1-2 drops of one of the above reagents. If the material is sufficiently basic, one of the above described color reactions will take place.

Positive reactions are obtained with such compounds as hydrated aluminum oxide, aluminum phosphate, barium oxide, barium carbonate, beryllium oxide, beryllium carbonate, calcium oxide, calcium carbonate, calcium phosphate, cadmium oxide, calcium hydrogen phosphate, ceric hydroxide, hydrated ferric oxide, magnesium oxide, magnesium carbonate, magnesium ammonium phosphate, magnesium phosphate, magnesium arsenate, magnesium ammonium arsenate, lead hydroxide, lead oxide, lead carbonate, and zinc carbonate.

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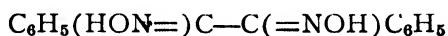
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 **$\alpha$ -BENZILDIOXIME**Synonym:  $\alpha$ -Diphenylglyoxime $C_{14}H_{12}O_2N_2$ 

Mol. Wt. 240.25

Beil. Ref. VII, 760.

**Use:** Detection of nickel and palladium.

Determination of nickel.

$\alpha$ -Benzildioxime consists of white microcrystalline leaflets, which melt at 235-237° C. with decomposition. It is almost insoluble in water, ether and glacial acetic acid, and is only slightly soluble in alcohol. It dissolves readily in sodium hydroxide solutions and in acetone.

**Preparation:** Dissolve 10 g. of benzil in 50 ml. of methyl alcohol and add 8 g. of hydroxylamine hydrochloride. Boil the mixture for 3 hours and filter. Wash the precipitate of  $\alpha$ -benzildioxime with hot water, and then with a small quantity of 50 per cent ethyl alcohol. Purify by recrystallizing from acetone.<sup>1,2</sup>

**Detection of nickel.**  $\alpha$ -Benzildioxime was first used by Tschugaeff<sup>3</sup> for the detection of nickel, with which it reacts to form a red nickel compound. This reaction was further studied by Attack,<sup>1,4-6</sup> who proposed the use of the reagent for the gravimetric determination of nickel. Like the nickel derivative of other  $\alpha$ -orthodioximes, nickel  $\alpha$ -benzildioxime consists of two molecules of oxime and one atom of nickel. The composition for this compound corresponds to the formula  $(C_{14}H_{11}O_2N_2)_2Ni$ . It is a true inner-complex and is insoluble in neutral and ammoniacal solutions, but dissolves readily in mineral acids and solutions of cyanides.

$\alpha$ -Benzildioxime appears to be superior to dimethylglyoxime for the nickel determination, since the nickel derivative of the former is less soluble. This also makes possible a more sensitive qualitative test. Further,  $\alpha$ -benzildioxime has the greater molecular weight, and consequently the percentage of nickel in the nickel precipitate is smaller; hence, the nickel factor is more suitable for an accurate determination.  $\alpha$ -Benzildioxime is very insoluble in water<sup>8</sup> and only slightly soluble in alcohol, and consequently extreme caution must be used to avoid the addition of a large excess of the reagent, since the compound itself may be precipitated upon the dilution of alcohol with water.

In the absence of interfering substances,  $\alpha$ -benzildioxime yields an immediate precipitate with as little as 0.002 mg. of nickel in 5 ml. of solution. This

corresponds to a sensitivity of less than 1 part in 2,000,000. An immediate and distinctive test for nickel is obtained with 10 ml. of an ammoniacal solution containing 1 p.p.m. of nickel and 100 p.p.m. of cobalt. For the detection of nickel in the presence of cobalt,  $\alpha$ -benzildioxime is definitely superior to dimethylglyoxime, since the color which the former reagent gives with cobalt is only a faint yellow in contrast to the dark brown cobalt dimethylglyoxime derivative. Further, nickel precipitates immediately, and there appears to be no solvent effect due to cobalt salts as is the case in testing with dimethylglyoxime. Interference by large quantities of cobalt may be eliminated by oxidation before applying the test.<sup>1,9</sup> Large quantities of silver, magnesium, chromium, zinc or manganese do not interfere with the test for nickel. Large quantities of nitrate, however, interfere.  $\alpha$ -Benzildioxime yields a violet color with ferrous salts, but this does not mask the reaction with nickel. The addition of tartrate or citrate prevents the precipitation of ferric iron, and in this way nickel may be detected in the presence of 1000 times as much iron.

The reagent recommended by Atack<sup>1</sup> is a 0.02-0.05 per cent solution of  $\alpha$ -benzildioxime in alcohol or acetone. The oxime is not very soluble in alcohol, but dissolves somewhat more readily if about 5 per cent ammonia is added. The ammoniacal solution is quite stable and keeps for some time, although the acetone solution is more easily prepared.

$\alpha$ -Benzildioxime has been used as a confirmatory test for nickel in a number of schemes of analysis,<sup>10,11</sup> and is recommended as one of the more satisfactory reagents by Wenger and co-workers.<sup>12</sup>

**Determination of nickel.** Because of the very slight solubility of the nickel derivative of  $\alpha$ -benzildioxime, this reagent is satisfactory for the gravimetric determination of nickel. The nickel precipitate is very bulky, however, and consequently not more than 25 mg. of nickel can be precipitated satisfactorily. The precipitation is carried out in an ammoniacal solution by the addition of  $\alpha$ -benzildioxime, with special care that only a very slight excess of the reagent is added. According to Peshkova<sup>13</sup> there is less danger of forming an impure precipitate when an alcoholic solution of  $\alpha$ -benzildioxime is used. The nickel precipitate is extremely insoluble and may be washed with hot water and water-alcohol mixtures. The following procedure may be used for the determination of nickel:

**Procedure.** Make the solution containing not more than 25 mg. of nickel slightly ammoniacal, and then add with stirring a slight excess of a 0.02 per cent alcoholic or acetone solution of  $\alpha$ -benzildioxime. Heat for a few minutes to coagulate the precipitate, and filter. If the precipitate is to be weighed after drying as nickel  $\alpha$ -benzildioxime, filter on a Gooch crucible using suction. Wash first with warm 50 per cent alcohol, and then with hot water, and finally dry at 110° C. Weigh as nickel  $\alpha$ -benzildioxime. The factor for nickel is 0.1092.

If the precipitate is to be ignited to nickel oxide, filter the precipitate on paper and wash well with hot water. Transfer to a porcelain crucible, moisten with nitric acid, and then ash. Cool, add 2-3 drops of nitric acid, evaporate the acid, and ignite and weigh as nickel oxide.



Nitrates interfere somewhat with the precipitation of nickel, and must be removed by evaporation with sulfuric acid before adding the reagent.

If cobalt is present, a sufficient quantity of  $\alpha$ -benzildioxime must be added to combine with both cobalt, which forms a soluble compound, and with nickel. Cobalt does not otherwise interfere.<sup>9</sup> The separation of nickel from iron by precipitation from an ammoniacal citrate or tartrate solution gives satisfactory results. Zinc and magnesium do not interfere with the precipitation of nickel if a sufficient quantity of ammonium salt is added to prevent their precipitation when the solution is made ammoniacal.<sup>14,15</sup> To prevent contamination of the nickel precipitate when formed in the presence of chromic salt, add 0.25 g. of potassium acid tartrate and 0.2 ml. of a 10 per cent cupric ammonium chloride,  $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl}$ , solution.<sup>16</sup> If manganese is present, nickel must be precipitated from a slightly acid solution containing acetic acid, although care must be exercised in this precipitation, since  $\alpha$ -benzildioxime is changed by acids into its  $\beta$ -isomer, which does not precipitate nickel.<sup>17</sup> Grossmann and Mannheim<sup>14,15</sup> suggest keeping manganese in solution by means of citric acid and a little hydrazine to prevent oxidation. Copper is kept in solution by means of Rochelle salt, but only a small proportion of copper should be present.

The gravimetric method for determining nickel with  $\alpha$ -benzildioxime has been thoroughly tested by Attack,<sup>1,4-6</sup> using known quantities of pure nickel salts ranging in quantity up to 25 mg., and both in pure solution and in the presence of cobalt and iron. The results are reported to be uniformly good, with the error always less than 0.1 mg. of nickel. This procedure has been further studied by Grossmann and Mannheim<sup>14,15</sup> and by Strebing<sup>18-20</sup> who report that Attack's method is reliable for small quantities of nickel. Strebing, however, reports consistently high results when the nickel complex is weighed directly, although the error is somewhat less when an acetone solution of  $\alpha$ -benzildioxime is used. The error reported by this procedure is from 0.1-0.2 mg. of nickel. The high results appear to be due to the contamination of the precipitate by the reagent, since correct values were obtained when the precipitate was ignited to the oxide before weighing. Strebing<sup>18-20</sup> recommends the latter procedure, although according to Attack ignition of the precipitate gives unsatisfactory results.

According to Strebing, the precipitation of nickel with  $\alpha$ -benzildioxime is unsuitable for microanalytical purposes, since results are consistently too high.

Fairhall<sup>21</sup> has recommended the use of  $\alpha$ -benzildioxime for determining nickel in biological materials. In this procedure the reagent is used to precipitate nickel from solutions containing interfering ions, and then after dissolving the precipitate in hydrochloric acid, the nickel is determined colorimetrically with potassium dithiooxalate.

Mironoff<sup>22</sup> suggests precipitating nickel with  $\alpha$ -benzildioxime, and then determining the nickel indirectly by the method of Tougarinoff.<sup>23</sup> The details of this procedure are described in the section on dimethylglyoxime (page 197).

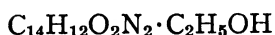
**Detection of palladium.** The palladium complex of  $\alpha$ -benzildioxime apparently decomposes rather rapidly, although Dwyer and Mellor<sup>7</sup> recommend

the use of the  $\beta$ -isomer, which is formed in an acid solution, for the detection of as little as  $3\gamma$  of palladium in 1 ml. of solution.

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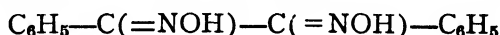
### $\gamma$ -BENZILDIOXIME

Synonym: Amphibenzildioxime



Mol. Wt. 286.32

Beil. Ref. VII, 763.



**Use:** Detection of nickel.

$\gamma$ -Benzildioxime is obtained as needle-like crystals from alcohol. The compound melts at  $100^\circ\text{C}$ . and loses its alcohol of crystallization, and then becomes a solid, and melts a second time at  $164$ - $166^\circ\text{C}$ . and is converted into the  $\beta$ -dioxime. It is insoluble in water, but is more soluble in water than the  $\beta$ -isomer.

**Preparation:** Dissolve 1 part of  $\beta$ -benzilmonoxime (M.P. =  $113$ - $114^\circ\text{C}$ .) and 4 parts of sodium hydroxide in sufficient cold water to form a clear solution. Add 2 parts of hydroxylamine hydrochloride and allow the mixture to stand for two days. Dilute with water, filter, and acidify strongly with dilute hydrochloric acid, but avoid any considerable rise in temperature. The reddish-white mass which forms consists essentially of the  $\gamma$ -dioxime. Filter with suction and press out most of the liquid, and then shake the residue vigorously with about 10 times its quantity of cold alcohol. The  $\alpha$ -dioxime is not dissolved. Filter and allow the filtrate to evaporate spontaneously. The first crystals to form on the walls of the dish are impure, while the solid which separates on the bottom of the

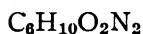
dish is pure. Remove this by filtration, and recrystallize from alcohol and press between filter paper.<sup>1</sup>

**Reaction with nickel.** Nickel salts react with  $\gamma$ -benzildioxime in an ammoniacal solution to form a yellow compound. In this reaction the oxime appears to act as a dibasic acid. The yellow color of the compound is in marked contrast to the deep red of the nickel inner-complex salts of the  $\alpha$ -dioximes in which the nickel is bound to the oxime nitrogen only.<sup>2</sup>

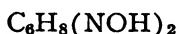
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### CYCLOHEXANEDIONEDIOXIME

Synonym: Nioxime



Mol. Wt. 142.14



**Use:** Detection of nickel.

Cyclohexanedionedioxime is a white crystalline compound which melts at 187-188° C. with decomposition.

**Preparation:** Dissolve 20 g. of cyclohexanone in 4 times its volume of glacial acetic acid and cool at 0° C. by immersing in ice water. Then add at one time 4 moles of bromine. Mix well, remove a few ml. of the mixture, warm until a lively reaction occurs and then add this to the ice-cooled mixture. When treated in this way, bromination of cyclohexanone occurs without too great an evolution of heat. Pour the reaction mixture into ice water and remove any unchanged bromine with a little sulfurous acid. Cool, separate the liquid dibromide and allow to crystallize. The melting point is 106-107° C. *Caution:* Do not let this compound come in contact with the skin.

Dissolve the crystalline dibromocyclohexanone by shaking with a potassium hydroxide solution, and acidify with sulfuric acid. Extract the mixture with ether, remove the ether, and distill the residue in vacuo as long as the distillate comes over colorless. By cooling to a low temperature, the distillate solidifies to a crystalline mass. Press out and recrystallize from petroleum ether. Dissolve this compound in an excess of potassium hydroxide and add an excess of hydroxylamine hydrochloride. Warm for 15 minutes on a water-bath and then pass into the cooled solution a current of carbon dioxide. Filter and recrystallize from water. More of the compound may be recovered by extracting the mother liquor with ether.<sup>1-3</sup>

The yield obtained by this method is very poor, although a sufficient quantity of the oxime is obtained to give a qualitative test with nickel. Rauh, Smith, Banks and Diehl<sup>4</sup> have prepared the oxime from 1,2-cyclohexandione, which is obtained by the oxidation of cyclohexanone by selenium dioxide.<sup>5</sup>

**Preparation:** Place 250 g. of cyclohexanone in a 1-liter 3-necked flask, which is equipped with a thermometer, reflux condenser and a dropping funnel.

Heat the liquid to 70-80° C. and add a solution of 280 g. of selenium dioxide in 1500 ml. of 95 per cent alcohol from the dropping funnel. About 2 hours are required for the addition of this solution, and the temperature of the reaction mixture should be maintained at 70-80° C. during this time. After all the selenium dioxide has been added, reflux the mixture for an additional 2 hours. Distill off as much of the liquid as possible, and decant the remainder from the elementary selenium. Wash the selenium with several portions of ether, and add the extracts to the principal portion of the liquid. Remove the ether by distillation, and distill the residual liquid at 25 mm. pressure. About 200 ml. of an oily liquid is obtained. Dissolve this oil in 1 liter of ether and extract 3 times with ice-cold, 10 per cent potassium hydroxide solution. Use a portion of the potassium hydroxide solution equivalent to 1.5 times that necessary to react with all the oil, which is assumed to be pure dione in the mono-enol form. Shake the alkaline extract once with ether to remove any unchanged cyclohexanone, acidify with ice-cold hydrochloric acid, and then saturate with salt. Extract the hydrochloric acid solution with ether, and dry the ether extract over anhydrous magnesium sulfate. Remove the ether by distillation, and distill the residual oil under vacuum. About 55 g. of oil is obtained. This is pale green in color and boils at 96-97° C. at 25 mm. All steps in the above procedure should be carried out in the shortest possible time and at a temperature of 0° C.

Convert the dione to the oxime immediately as follows: Dissolve 55 g. of 1,2-cyclohexandione in 500 ml. of water. Cool the solution to 0° C., and dissolve in it 170 g. of hydroxylamine hydrochloride. Dissolve 225 g. of potassium hydroxide in 1 liter of water, cool to 0° C., and add dropwise and with constant stirring over a period of 15 minutes to the solution of cyclohexandione and hydroxylamine hydrochloride. Heat the mixture for 2 hours on a steam bath, cool to 0° C., neutralize with dry ice, saturate with salt, and filter. Wash the product on the filter once with a small portion of ice-cold water, and then recrystallize from water.

Cyclohexanedioxime may also be obtained by the synthesis of 2-isonitrosocyclohexanone-1 by the action of an alkyl nitrite on cyclohexanone,<sup>8</sup> and the subsequent oximation of the isonitroso compound.<sup>4</sup>

**Detection of nickel.** Cyclohexanedioxime is the cyclic analog of dimethylglyoxime, and like the latter yields an intense red nickel derivative, which is insoluble in neutral and ammoniacal solutions, but is decomposed by mineral acids.<sup>2,3,7</sup>

Cyclohexanedioxime was first prepared and studied by Wallach,<sup>2,8,7</sup> who proposed its use for the qualitative detection of nickel. The test may be carried out as a drop reaction, in test tube or as a spot test.<sup>2,3,8,9</sup> According to Wallach, the test is obtained with 1 part of nickel in 2,000,000 parts of a slightly ammoniacal solution. A red coloration is first obtained and after a few hours a red precipitate forms. Cyclohexanedioxime reacts with cobalt to give a brownish-yellow coloration which does not interfere with the nickel detection.

Unlike dimethylglyoxime, cyclohexanedioxime is soluble in water. This is a highly important characteristic, since an aqueous solution of the reagent

can be used for the precipitation of nickel without danger of contaminating the nickel compound, as is the case when dimethylglyoxime is used. The higher molecular weight of cyclohexanedionedioxime is also advantageous, since the nickel compound of cyclohexanedionedioxime contains only 17.21 per cent of nickel.

The use of cyclohexanedionedioxime as a quantitative reagent has not thoroughly been investigated, although preliminary experiments indicate that nickel is completely precipitated. A 0.02 per cent aqueous solution is suitable as an analytical reagent.

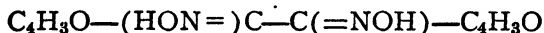
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### $\alpha$ -FURILDIOXIME

$C_{10}H_8O_4N_2$

Mol. Wt. 220.18

Beil. Ref. XIX, 166.



**Use:** Detection and determination of nickel and platinum.

$\alpha$ -Furildioxime consists of white needle-like crystals, which melt at 166-168° C. It is very soluble in alcohol and ether.

**Preparation:** *Furoin:* Dissolve 40 parts of furfural in 30 parts of alcohol and 80 parts of water, and mix with 4 parts of potassium cyanide, and then heat for 30-40 minutes in a flask fitted with a reflux condenser. Filter off the reddish crystalline solid, and wash with water to remove the colored product. Shake several times with a small quantity of cold alcohol, and each time free the solid from the brown alcoholic solution by filtering with suction. The pale yellow solid which is thus obtained is dried between sheets of filter paper, and is then dissolved in a little boiling toluene with an equal volume of alcohol and allowed to cool. Furoin separates as a crystalline solid.

*Furil:* Dissolve 1 part of furoin in 12 parts of hot alcohol, cool quickly, and dissolve the separated crystalline mass in the least possible quantity of sodium hydroxide. Add to this solution an equal volume of water, and cool to 0° C. Pass through this mixture a vigorous stream of air until the greenish-blue color is completely changed to a dirty brown. Furil separates in the form of fine needles. The separation is more complete if water is added. Filter, wash the precipitate well with water, and crystallize from boiling alcohol.<sup>1</sup>

*Furildioxime:* Heat furil on a water bath for a few hours with 8 times its weight of alcohol and an excess of hydroxylamine hydrochloride until solution

is complete. Pour this solution into 6 times its volume of boiling water, keep at the boiling point for a few minutes, and then allow to cool. Filter the solution from the precipitate, which is essentially furil, and allow to stand over sulfuric acid. After a short time the oxime separates in the form of prisms. Crystallize from water containing a little animal charcoal.<sup>2</sup>

**Detection and determination of nickel.**  $\alpha$ -Furildioxime reacts with ammoniacal solutions of nickel salts to yield an amorphous red precipitate of nickel furildioxime. This compound is similar in composition to that of the other dioximes.

This reaction is more sensitive than that with dimethylglyoxime or with  $\alpha$ -benzildioxime, and may be used satisfactorily for the detection and determination of nickel. The reagent is sufficiently soluble in hot water to make possible the use of an aqueous solution in the reaction for nickel. Nickel may be determined by weighing the precipitate directly, or after ignition to NiO, or the nickel content of the  $\alpha$ -furildioxime may be determined by electrolysis, or by titration with potassium cyanide.<sup>3-5,9</sup>

The following procedure may be used for detecting nickel:

**Reagent.** Dissolve approximately 2 g. of  $\alpha$ -furildioxime in 100 ml. of hot water, or in sufficient warm alcohol to yield a 10-15 per cent solution.

**Procedure:** Add ammonium hydroxide to a solution of the substance to be tested until the mixture is faintly ammoniacal, and then add a few drops of the reagent. A red precipitate forms if nickel is present. The sensitiveness of this reaction is 1:6,000,000.

Ferrous iron is the only other common cation which gives a precipitate with  $\alpha$ -furildioxime, and this occurs only when a considerable quantity of the ferrous ion is present. If cobalt is present, the ammoniacal solution must be oxidized with hydrogen peroxide to prevent interference. No precipitate is obtained with silver, copper or zinc, and manganese gives a negative reaction. Ferric iron, chromium, and aluminum do not give a reaction in ammoniacal solutions containing a citrate or tartrate. Platinum and palladium are precipitated by the reagent.

The precipitation of nickel with  $\alpha$ -furildioxime is quantitative, and consequently may be used for the gravimetric determination of nickel.<sup>3</sup>

**Procedure:** Dilute the sample containing 0.02 g. of nickel to 100 ml., make faintly alkaline with ammonia, and then add an excess of a 2 per cent aqueous solution, or a 10 per cent alcoholic solution of the reagent. Filter the amorphous red precipitate which is formed, and wash well with warm water. Transfer the paper and contents to a beaker and treat with 1:1 nitric acid. Filter off the paper pulp, wash, add sulfuric acid to the filtrate, and evaporate. Dilute the solution somewhat, make ammoniacal, and determine nickel by electrolysis. As an alternative procedure, the paper may be dried at 120-130° C. and weighed, or the precipitate may be ignited to NiO in a covered crucible. The precipitate has the formula  $C_{22}H_{14}N_4O_8Ni$ , and contains 11.85 per cent nickel.

Harwood and Theobald <sup>6</sup> have used  $\alpha$ -furildioxime for the determination of small quantities of nickel in rock.

**Determination of platinum.** Ogburn (7) has proposed a method for the separation and detection of the platinum metals using  $\alpha$ -furildioxime to precipitate platinum. According to this procedure, palladium is precipitated with dimethylglyoxime, and after filtration platinum is obtained from the filtrate by precipitating with  $\alpha$ -furildioxime. Rhodium is precipitated as  $K_3Rh(NO_2)_6$ , and iridium and osmium are precipitated as the metal.

Platinum is determined in this procedure as follows: <sup>7,8</sup>

**Procedure.** After precipitating palladium with dimethylglyoxime, and after its removal by filtration, the filtrate, which contains platinum, rhodium, ruthenium, osmium, and iridium, is treated with a 2 per cent alcoholic solution of  $\alpha$ -furildioxime and a quantity of alcohol equivalent to 10 per cent of the total volume. Then boil for 30 minutes. A large excess of the reagent should be avoided. Filter the hot mixture with slight suction, and wash the precipitate with small portions of cold water containing a few ml. of alcohol until the washings are colorless. Dry the precipitate and carefully ignite, first in air and then in hydrogen. Cool, and weigh as metallic platinum.

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## BENZOYLMETHYLGLYOXIME

$C_{10}H_{10}O_3N_2$

Mol. Wt. 206.18



**Use:** Determination of palladium.

This reagent occurs as white needles. It melts at 178° C., and decomposes with the evolution of gas. It is soluble in alcohol and cold water.

**Preparation: Isonitrosobenzoylacetone:** Dissolve 1 atomic weight of sodium in alcohol and add 1 molecular weight of purified benzoyl acetone. Cool well and add nitrous acid until the reaction is neutral. Dilute with considerable water, filter, dissolve the residue in dilute sodium hydroxide, and precipitate with carbonic acid. Crystallize two times from hot water and purify with animal charcoal.

**Benzoylmethylglyoxime:** Mix 1 mole of isonitrosobenzoylacetone with 2 moles of hydrochloric acid and 2 moles of hydroxylamine, and then allow the mixture to stand for 24 hours. Warm slightly, and add water. Extract with ether, and allow the ether extract to evaporate. Crystallize several times from hot water containing animal charcoal. Then dissolve in a little sodium hydroxide and precipitate with ammonium carbonate.<sup>1</sup>

**Determination of palladium.** Benzoylmethylglyoxime appears to be a specific reagent for palladium, with which it reacts to form a yellow precipitate which is similar in composition to the other metal salts of the dioximes. Since precipitation is quantitative, this reaction may be used for the gravimetric determination of palladium.

**Procedure.** Make 100-200 ml. of the solution to be analyzed acid with hydrochloric acid, and add a 2 per cent alcoholic solution of benzoylmethylglyoxime in 40 per cent excess. Boil for a few minutes and allow the mixture to stand for 12 hours. Filter, wash with dilute hydrochloric acid, and then with water. Dry at 105° C. and weigh. The factor for palladium is 0.2054.

The yellow precipitate is soluble in ammonium hydroxide, but is insoluble in water and dilute hydrochloric acid. If platinum, iridium, osmium, rhodium, or gold is present add 1 to 6 ml. of hydrochloric acid to the solution before adding the reagent. Add tartaric acid if antimony is present, and if molybdenum, tungsten, and vanadium are present, the addition of monopotassium phosphate and hydrochloric acid is necessary. Bismuth, cadmium, mercury, arsenic, tin, iron, nickel, cobalt, and zinc do not interfere if hydrochloric acid is present.<sup>2,3</sup>

Holzer,<sup>4</sup> who has used dimethylglyoxime for the determination of palladium, suggests that benzoylmethylglyoxime is somewhat more satisfactory as a reagent. Benzoylmethylglyoxime is suitable for the detection of palladium in jewelry metal.<sup>5</sup>

1. M. Ceresole, *Ber.* 17, 812 (1884).

2. H. Grisolle and M. Servigne, *Ann. chim. anal. chim. appl.* 12, 321-31 (1930); *C.A.* 25, 261 (1931).

3. J. Hanus, A. Jilek, and J. Lukas, *Chem. News.* 131, 401-2 (1925); 132, 1-4 (1926); *C.A.* 20, 1368 (1926).

4. H. Holzer, *Z. anal. Chem.* 95, 392-400 (1933); *C.A.* 28, 1627 (1934).

5. F. Durdik, *Chem. Listy.* 20, 406-7 (1926); *C.A.* 21, 1944 (1927).

## BENZYLMETHYLGLOXIME

$C_{10}H_{12}O_2N_2$

Mol. Wt. 192.20

Beil. Ref. VII, 685.



**Use:** Detection of nickel and palladium.

This reagent is a colorless crystalline compound melting at 194° C. It is soluble in acetone and ethyl alcohol.

**Preparation:** *Monoxime of benzylmethylglyoxal:* Add concentrated hydrochloric acid to a mixture of 1 mole of benzyl acetoacetate and 1.1 mole of sodium



nitrite dissolved in 1.2 moles of 10 per cent sodium hydroxide. Keep the temperature below 10° C. Collect the oily material on a tile, and then crystallize from dilute alcohol.

**Dioxime of benzylmethylglyoxal:** Heat together on a water bath one mole of the monoxime, 1.2 moles of hydroxylamine hydrochloride and 2.5 moles of 20 per cent sodium hydroxide, and then precipitate the oxime with acetic acid. Recrystallize the product from 80 per cent acetic acid. The colorless crystals melt at 194° C.<sup>1</sup>

**Reactions:** Nickel and palladium compounds of benzylmethylglyoxime are prepared as follows: dissolve the reagent in acetone or alcohol and add to a cold aqueous solution of nickel chloride (free from iron and cobalt), and then add sodium acetate in the ratio of 2.5 moles of the acetate to 2 moles of the glyoxime. The nickel compound forms as a bright orange precipitate, and exists in two isomeric forms.<sup>1</sup>

Palladium also forms two isomeric compounds which are orange in color.<sup>2</sup>

1. S. Sugden, *J. Chem. Soc.* 135, 246-50 (1932); *C.A.* 26, 2186 (1932).
2. F. P. Dwyer and D. P. Mellor, *J. Am. Chem. Soc.* 57, 605 (1935).

## OXALENEDIAMIDOXIME



Mol. Wt. 118.07

Beil. Ref. II, 557 (240).



**Use:** Detection and determination of nickel.

The reagent is obtained as colorless prisms from water. It melts with slight evolution of gas at 196° C. The compound is readily soluble in hot water, but only slightly soluble in cold water and alcohol. It is very slightly soluble in ether, chloroform and benzene, but dissolves readily in acids and bases.

**Preparation:** Dissolve one molecular weight of hydroxylamine hydrochloride in water, add one molecular weight of potassium hydroxide, and then pass cyanogen gas through the ice-cold solution. Filter off the crystals which form, and evaporate the filtrate to obtain more of the compound. Purify by crystallizing from hot water.<sup>1</sup>

**Detection and determination of nickel.** Oxalenediamidoxime has been used for the estimation and separation of nickel. As a precipitant for nickel it possesses the advantage of being more soluble in hot water than dimethylglyoxime. Nickel is precipitated by adding the reagent to a faintly ammoniacal solution containing ammonium chloride. The nickel compound is light orange in color and corresponds to the formula  $\text{Ni}(\text{C}_2\text{H}_5\text{O}_2\text{N}_4)_2 \cdot 2\text{H}_2\text{O}$ . The nickel precipitate can be weighed after drying at 110-120° C. The anhydrous compound contains 20.02 per cent of nickel. Excellent results are obtained with samples containing 0.006-0.024 g. of nickel.

Oxalenediamidoxime also serves to separate nickel from zinc and from cobalt. This is accomplished, if not more than 0.05 g. of cobalt is present, by

adding about 1 g. of hydroxylamine hydrochloride to the solution containing the reagent before making alkaline with ammonia.<sup>2</sup>

1. E. Fischer, *Ber.* **22**, 1931 (1889).

2. R. Chatterjee, *J. Indian Chem. Soc.* **15**, 608-10 (1938) ; *C.A.* **33**, 2841 (1939).

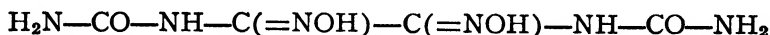
### OXALENEDIURAMIDOXIME

Synonym: Dicarbamidoglyoxime

$C_4H_8O_4N_6$

Mol. Wt. 204.10

Beil. Ref. III, 65.



**Use:** Detection and determination of nickel.

Separation of nickel from cobalt.

Oxalenediuramidoxime is obtained as needles from dilute alcohol. It melts with decomposition at 191-192° C. It is insoluble in cold water, ether, chloroform and benzene, but is easily soluble in alcohol, acids and alkalies.

**Preparation:** Prepare diaminoglyoxime by treating a cold alkaline solution of hydroxylamine hydrochloride with cyanogen gas.<sup>1</sup> Treat 1 mole of the recrystallized product with 2 moles of hydrochloric acid ( $d = 1.19$ ), and then with an aqueous solution containing 2 moles of potassium cyanate. Purify the crystalline mass by crystallizing from hot water.

Prepare the nickel reagent by dissolving a considerable quantity of the oxalenediuramidoxime in hot dilute ammonium hydroxide. Cool and filter. The filtrate, which contains the ammonium salt of the dioxime, is used as the reagent for nickel.<sup>2,3</sup>

**Detection and determination of nickel.** Nickel may be detected or determined by means of the orange-colored precipitate which forms when a solution of the ammonium salt of oxalenediuramidoxime is added to an ammoniacal solution containing a nickel salt.<sup>2,4,5</sup> Since oxalenediuramidoxime contains the nickel-specific dioxime group, the structure of the nickel compound might be expected to resemble that of the nickel complex of dimethylglyoxime. It has been shown, however, that the reagent functions as a dibasic acid and forms normal salts. The nickel salt forms an addition compound with ammonia.

The use of oxalenediuramidoxime in precipitations where the presence of alcohol might be objectionable offers some advantages, but otherwise dimethylglyoxime is probably preferable.

**Procedure.** To determine nickel, make the solution to be analyzed alkaline with ammonium hydroxide, add an excess of the reagent, and then boil for 2 minutes. Allow the mixture to cool, filter through a Gooch crucible, wash with cold water, dry at 110-113° C., and weigh. The factor for nickel is 0.1992.

One part of nickel in 150,000 parts of water may be detected by a similar procedure.

**Separation of nickel from cobalt.** In a strongly ammoniacal solution, nickel can be separated from cobalt by precipitation with oxalenediuramidoxime. Excellent results are obtained with a nickel-cobalt ratio ranging from 1:0.28 to 1:2.8.

1. E. Fischer, *Ber.* **22**, 1931 (1889).
2. F. Feigl and A. Christiani-Kronwald, *Z. anal. Chem.* **65**, 341-5 (1925); *C.A.* **19**, 1833 (1925).
3. W. Zinkeisen, *Ber.* **22**, 2952 (1889).
4. G. Gutzeit, *Helv. Chim. Acta.* **12**, 722 (1929).
5. H. Grisolle and M. Servigne, *Ann. chim. anal. chim. appl.* **12**, 321-31 (1930); *C.A.* **25**, 261 (1931).

## PHENYLGLYOXIME



Mol. Wt. 164.14

Beil. Ref. VII, 672.



**Use:** Determination of copper and nickel.

Phenylglyoxime is a crystalline solid melting at 168° C. It is soluble in alcohol and ether, but is only very slightly soluble in chloroform and benzene.

**Preparation:** Mix 1 mole of sodium isonitrosoacetophenone with 1 mole of hydroxylamine hydrochloride and 1 mole of sodium hydroxide in an aqueous solution, and allow to stand for 1 hour at ordinary temperature. Precipitate with acetic acid, filter with suction, wash with chloroform and recrystallize from ether.<sup>1,2</sup>

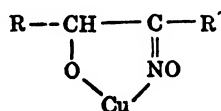
**Determination of copper and nickel.** Mironoff<sup>3</sup> has found that the titrimetric method of Tougarinoff<sup>4</sup> gives quantitative results when small quantities of copper and nickel are precipitated with phenylglyoxime. The procedure employed is the same as that with dimethylglyoxime (page 197).

1. A. Russanow, *Ber.* **24**, 3501 (1891).
2. H. Wieland and L. Semper, *Ann.* **358**, 57 (1908).
3. J. Mironoff, *Bull. soc. chim. Belg.* **45**, 1-8 (1936); *C.A.* **30**, 6672 (1936).
4. M. B. Tougarinoff, *Ann. soc. sci. Bruxelles.* **54B**, 314 (1934); *C.A.* **29**, 1748 (1935).

## CHAPTER VII

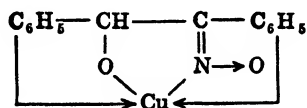
### ACYLOIN OXIMES

A number of compounds containing the group  $>\text{C}(\text{OH})-\text{C}(=\text{NOH})-$  possess valuable analytical properties. These substances, which are known as the  $\alpha$ -acyloin oximes, react with cupric salts to form green, water-insoluble complexes. There is some difficulty in assigning a definite structure to the copper complex, since available evidence indicates that 3 structures are possibly correct: In reacting with copper, the molecule may act as a dibasic acid in which both hydroxyl and oxime groups are acidic, or it may function as a monobasic acid with either the hydroxyl or oxime group reacting as an acid with the other serving as a coordinating group. Available evidence seems to indicate, however, that the  $\alpha$ -acyloin oximes react as dibasic acids toward cupric salts to form compounds of the type



Under special conditions  $\alpha$ -benzoinoxime forms compounds with cobalt, nickel and with bivalent platinum and palladium, but in the formation of these substances the oxime functions as a monobasic acid.<sup>1</sup>

In the  $\alpha$ -acyloin oximes, only the structure  $=\text{C}(\text{OH})-\text{C}(=\text{NOH})-$  is regarded as the copper-specific group, since the property of water-insolubility and the color of the cupric salt are independent of the character of the  $R$  and  $R'$  radicals. The nature of these radicals, however, influences the reaction of the copper salt with ammonia. If  $R$  and  $R'$  are capable of forming coordinate bonds with the copper atom, the copper compounds exhibit the character of true inner-complex salts, which are incapable of adding ammonia, and are insoluble in ammonia. Aromatic radicals, such as phenyl, benzyl and furoyl form coordinate bonds with the copper atom. Undoubtedly in the copper salts of the  $\alpha$ -acyloin oximes containing these radicals, insolubility in ammonia results from the saturation of the coordination capacity of the copper atoms by the aromatic radicals. On the basis of this conception, Feigl has assigned the following structure to the copper salt of  $\alpha$ -benzoinoxime:

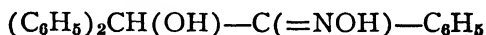


It is a further interesting fact that symmetrical and unsymmetrical  $\alpha$ -acyloin oximes react similarly. For example, the substitution of the methoxy, isopropyl, or methylene dioxy radicals in the phenyl group of  $\alpha$ -benzoinoxime is without effect upon the salt-forming properties of the oxime.

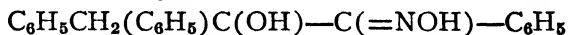
The compound phenylhydroxyacetamidoxime,  $\text{C}_6\text{H}_5\text{—CH(OH)—C(=NOH)—NH}_2$ , like other  $\alpha$ -acyloin oximes, forms an ammonia-insoluble copper salt, which indicates that the amine group has the same capacity of forming a coordinate bond with copper as does the phenyl group.

Some of the aliphatic acyloin oximes also form copper salts which are only slightly soluble in ammonia, and so it appears that some aliphatic radicals, such as pentyl, hexyl and heptyl, are capable of coordination with the copper atom.

Since many of the radicals in the ammonia-insoluble copper salts of the acyloin oximes contain a fairly large number of atoms, it might be inferred that the property of ammonia-insolubility is the result of a weighting effect of the molecule. The copper salt of  $\alpha$ -benzoinoxime, however, is insoluble in ammonia, while the copper salts of the phenyl and benzyl derivatives of this compound,



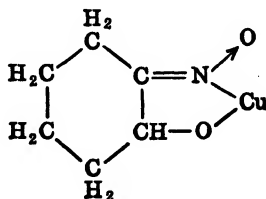
and



which have greater molecular weights, are soluble in the same medium. Undoubtedly in these compounds, the solubility of the copper salts in ammonia results from a mutual coordination between the two ring structures bound to the same carbon atom, whereby each loses its ability to form a coordinate bond with the copper atom. Thus it appears that the ability of the radicals  $R$  and  $R'$  to saturate the copper atom by coordination must determine the solubility of the copper salt in ammonia.

Hofmann and Küspert<sup>2</sup> prepared the compound  $\text{Ni(CN)}_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_6$ , and were able to show that a ring system containing a double bond is capable of coordination. Further, Feigl<sup>3</sup> has shown that phenylazoaldoximes of the type  $\text{R—C(=NOH)—N=N—C}_6\text{H}_5$  form green copper salts which are insoluble in ammonia, but only if  $R$  is aromatic or is an aliphatic radical containing more than 4 carbon atoms.

The group  $\text{=C(OH)—C(=NOH)—}$  reacts specifically with copper even though the 2 carbon atoms are a part of a ring structure. Thus, *o*-cyclohexanolone oxime forms a green, water-insoluble copper salt

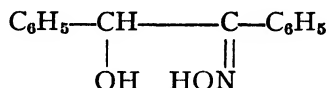


This compound is soluble in ammonia, however, since the ring structure is saturated and incapable of coordination with the copper atom.

It should be emphasized that not all hydroxy oximes give the copper reaction. For example, the oximes of pentanol-2-one-4,  $\text{CH}_3\text{—CH(OH)—CH}_2\text{—C(=NOH)—CH}_3$  and chloral acetophenone,  $\text{CCl}_3\text{—CH(OH)—CH}_2\text{—C(=NOH)}$

—C<sub>6</sub>H<sub>5</sub>, do not form water-insoluble copper salts. Since the structures of these compounds are such that the formation a 5-membered ring with copper is impossible, it may be inferred that the copper-specificity of the acyloin oximes depends in part upon a structure which makes possible the formation of such a ring. The acid character of the hydroxyl group is greatly increased by the proximity of the oxime group, and this relationship appears to be essential for the hydroxy oxime to function as a dibasic acid; hence, if the =C(OH)— and =C(=NOH)— groups are separated by a methylene group, as in the above compounds, a 5-membered ring closed with principal valences is not possible.

Finally, the ability of the acyloin oximes to form salts is dependent upon their steric configuration.  $\beta$ -Benzoinoxime,



for example, forms a water-insoluble copper salt, but it is brown in color and otherwise unlike the copper salt of the  $\alpha$ -isomer, and is probably differently constituted.

Of the many  $\alpha$ -acyloin oximes which have been studied, only  $\alpha$ -benzoinoxime is included in this section, since the others appear to offer no advantages in analytical procedures. Other acyloin oximes which have been investigated by Feigl<sup>4,5</sup> are:

Acetoinoxime	Cyclohexanolonoxime
Acetoloxime	<i>p</i> -Dimethylaminobenzoinoxime
Anisoinoxime	Diphenylacetoinoxime
Benzoanisoinoxime	Fructoseoxime
Benzofuroinnoxime	Furoinnoxime
Benzylbenzoinoxime	Oenanthoinoxime
<i>n</i> -Butyrolonoxime	Phenylbenzoinoxime
<i>n</i> -Caprolonoxime	Phenylhydroxyethenylamidoxime
4-Chlor-4'-dimethylaminobenzoinoxime	Piperonylloxime
Cuminanisoinoxime	Propionloxime
Cuminoxime	<i>n</i> -Valerionoxime

1. J. Jennings and Co-workers, *J. Chem. Soc.* **1935**, 818.
2. K. Hofmann and F. Küspert, *Z. anorg. allgem. Chem.* **15**, 204 (1897).
3. F. Feigl, *Oesterr. Chem.-Ztg.* **30**, 13 (1927).
4. F. Feigl, G. Sicher and O. Singer, *Ber.* **58B**, 2294-303 (1925).
5. F. Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, p. 81-3, Akademische Verlagsgesellschaft, Leipzig (1931).

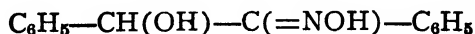
### $\alpha$ -BENZOINOXIME

Synonym: Cupron

C<sub>14</sub>H<sub>13</sub>O<sub>2</sub>N

Mol. Wt. 227.25

Beil. Ref. VIII, 175.



**Use:** Detection of copper, molybdenum and tungsten.

Determination of copper, molybdenum and tungsten.

$\alpha$ -Benzoinoxime consists of white crystals which darken on exposure to light. It melts at 149-151° C. It is only slightly soluble in water but dissolves readily in alcohol and aqueous ammonium hydroxide solution. The compound should be protected from light.

**Preparation.** *Benzoin:* Mix 10 g. of freshly distilled benzaldehyde and 25 ml. of alcohol with a solution of 2 g. of potassium cyanide in 5 ml. of water. Heat on a water-bath for 1 hour under reflux, and then allow the mixture to cool slowly. Filter the crystals which separate, wash with a little alcohol and dry on a water-bath. Purify by recrystallizing from alcohol. The melting point is 134° C.<sup>1</sup>

*$\alpha$ -Benzoinoxime.* Treat a mixture of 5 g. of benzoin and 20 g. of alcohol with an aqueous solution containing 4 g. of hydroxylamine hydrochloride that has previously been neutralized with 2.2 g. of sodium hydroxide. Boil the mixture for one and one-half hours under reflux, and then precipitate  $\alpha$ -benzoinoxime by treating with water. Filter the precipitate, dry and recrystallize from ether.<sup>2</sup>

**Detection of copper.** Benzoinoxime, like other acyloin oximes, reacts with cupric salts to form an insoluble, green precipitate. Although it has generally been accepted that in this reaction  $\alpha$ -benzoinoxime functions as a dibasic acid to form a compound in which the copper atom is bound by primary valences to the oxygen and nitrogen atoms of the hydroxyl and oxime groups respectively, other structures are possible in which the nitrogen atom or the oxygen atom may be bound to the copper atom by coordination.

Dubsky and Langer<sup>6</sup> have studied the formation of the copper compound of  $\alpha$ -benzoinoxime, and have arrived at the conclusion that the precipitate is actually a basic cupric salt which polymerizes readily into the corresponding diol salt.

The diol salt is not soluble in acetic acid and does not add ammonia, but it does adsorb ammonia and cupric hydroxide. Langer<sup>7</sup> suggests that possibly the copper salt possesses a dimeric structure.

The formation of the green copper salt is frequently used for the detection of small quantities of copper.<sup>3-5</sup> Since the copper compound is completely insoluble in ammonia, the test is usually carried out in an ammoniacal medium.

Interference due to the presence of other metallic salts which are precipitated by ammonia is prevented by the addition of sodium potassium tartrate. The copper test is less sensitive, however, in the presence of large quantities of the tartrate, and large quantities of ammonium salts also prevent the precipitation of the copper compound. For this reason solutions that are strongly acid or which contain ammonium salts should be evaporated and ignited and the residue dissolved in a little dilute hydrochloric acid before carrying out the  $\alpha$ -benzoinoxime test.

The following method may be used to detect small quantities of copper:

**Procedure.** Place a drop of the weakly acid solution to be tested on a strip of filter paper and add 1 drop of a 5 per cent alcoholic solution of  $\alpha$ -ben-

zoinoxime, and then hold the spot over a bottle of ammonium hydroxide. A green coloration appears if copper is present. In the presence of large quantities of other ions which may be precipitated by ammonium hydroxide, place a drop of 10 per cent sodium potassium tartrate solution on the filter paper before the addition of  $\alpha$ -benzoinoxime.

This test may be modified by using a test paper prepared by impregnating a good grade of quantitative filter paper with a saturated solution of  $\alpha$ -benzoinoxime, and applying the test solution to this paper.

By means of the above procedure, 0.1 $\gamma$  of copper can be detected at a concentration limit of 1:500,000.

If the solution to be tested is strongly acid, first place a drop of ammonium hydroxide on the filter paper and then a drop of the test solution and leave the paper for several minutes in a warm place. In this way, 0.5 $\gamma$  of copper can be detected in the presence of 1000 times as much hydrochloric acid.

Geilmann and Brunger<sup>8</sup> recommend the following procedure:

**Procedure.** Impregnate quantitative filter paper with a 5 per cent alcoholic solution of  $\alpha$ -benzoinoxime and allow to dry. Cut into strips 1 mm. wide and 10 mm. long, and then dip one of these strips into a warm drop of the solution to be tested. An appreciable green zone develops within a few minutes if copper is present, and when this is treated with ammonia the color is intensified. In this way as little as 0.05 $\gamma$  of copper can be detected.

Metallic salts generally do not interfere with this test, but high concentrations of neutral salts markedly decrease the sensitivity.

Korenman and Ditsent<sup>9</sup> recommend the following procedure for detecting copper in the presence of large quantities of most other cations:

**Procedure.** To 3-5 ml. of the solution to be tested add an equal volume of a saturated solution of Rochelle salt, and then add ammonium hydroxide until the solution is slightly alkaline. Then add a few drops of a saturated alcoholic solution of  $\alpha$ -benzoinoxime and shake well. Add 1 ml. of chloroform and again shake. A green coloration appears in the chloroform layer if copper is present. By this reaction 0.05-0.1 mg. of copper can be detected in the presence of a large excess of almost all other cations except nickel and cobalt.

Feigl<sup>3</sup> has used  $\alpha$ -benzoinoxime for the microdetection of copper:

**Procedure.** Place a drop of the copper solution on a glass slide, add a drop of alcoholic  $\alpha$ -benzoinoxime, and warm gently. The green precipitate of the copper compound may be observed microscopically. A little glycerol should be added to the test drop to prevent the evaporation of alcohol.

Thomson<sup>10</sup> has applied  $\alpha$ -benzoinoxime to a special technique of coloroscopic analysis for the detection of copper. He reports that by this method it is possible to detect 0.004 $\gamma$  of copper at a dilution of 1:500,000. Fritz<sup>11</sup> has studied the sensitivity of the copper test by an electro-spot method and reports that this method shows values somewhat lower than those reported using other methods. Jirkov-



osky<sup>12</sup> has used  $\alpha$ -benzoinoxime to detect copper in determining the purity of assay beads, and Agostini,<sup>13</sup> Davies,<sup>14</sup> and Dobbins and Southern<sup>15</sup> have used  $\alpha$ -benzoinoxime for the detection of copper in a systematic scheme of analysis.

Pavelka and Setta<sup>48</sup> have used  $\alpha$ -benzoinoxime for the microchemical detection of copper as an impurity in ammonium molybdate.

**Determination of copper.** Copper is quantitatively precipitated by  $\alpha$ -benzoinoxime from a boiling, ammoniacal solution, even in the presence of tartrate ions. Feigl<sup>5</sup> has used this reaction for the determination of copper.

**Procedure.** To a neutral solution containing very little, or preferably no ammonium salt, add dilute ammonium hydroxide carefully until a clear blue solution is obtained. Heat to boiling and add dropwise an alcoholic solution of  $\alpha$ -benzoinoxime until the blue color of the solution disappears. Filter through a Gooch crucible and wash the green precipitate of the copper compound with a hot, 1:100 ammonium hydroxide solution, and finally with hot water. Dry at 105-115° C. and wash with warm alcohol and then with water. Dry at 105-115° C. to constant weight. The factor for copper is 0.2202.

Isibasi<sup>16</sup> has studied the drying temperature of the copper compound and reports that the most suitable temperature is from 105° C. to 140° C.

Azzalin<sup>17</sup> has reported that the above method proposed by Feigl<sup>5</sup> is not reliable. He has found that the excess reagent cannot be completely washed from the precipitate, and because of this more satisfactory results can be obtained if the precipitate is ignited and weighed as cupric oxide. Under these conditions, however, there is a marked tendency to form graphite, but this cause of high results can be avoided by heating the precipitate very slowly. Employing this precaution the method appears to be about as accurate as the standard procedures, provided copper alone is present. The presence of iron, zinc, aluminum, lead or tin, however, may result in considerable error due to occlusion.

Shik<sup>18</sup> also reports that Feigl's method<sup>5</sup> is unsatisfactory, because it is impossible to avoid the precipitation of cupric oxide before the addition of  $\alpha$ -benzoinoxime. To remedy this, Shik<sup>18</sup> suggests that the copper solution containing Rochelle salt be heated to boiling and  $\alpha$ -benzoinoxime added, and that finally sufficient dilute ammonium hydroxide be added to impart a faint odor to the solution. Shik<sup>18</sup> further reports that the determination of copper in the presence of small quantities of zinc or iron is unsatisfactory.

Strebing<sup>19</sup> recommends the following micromethod for determining as little as 0.1 mg. of copper:

**Procedure.** To the solution in a test tube, add a slight excess of aqueous ammonium hydroxide and heat on a water-bath. Add dropwise 1-2 ml. of 1 per cent  $\alpha$ -benzoinoxime in alcohol, and allow the tube and contents to stand for 20 minutes in a boiling water-bath. If the supernatant liquid is not clear, too much ammonia has been added. Filter, wash with water containing ammonia and then with alcohol, and finally dry at 105° C. and weigh. The factor for copper is 0.2202.

Hecht and Reissner<sup>20</sup> have reported that reliable results are obtained using Strebinger's method. Nikitina<sup>21</sup> has used a similar method for the determination of copper in the products of corrosion of aluminum and magnesium alloys. Feigl<sup>22</sup> has used  $\alpha$ -benzoinoxime for the separation of copper from iron, aluminum and other metals precipitated by ammonium hydroxide. These separations are made possible by the fact that  $\alpha$ -benzoinoxime precipitates copper from ammoniacal solutions in the presence of tartrate or glycerol, while under these conditions iron and aluminum remain in solution.

Kar<sup>23</sup> has developed a procedure for using  $\alpha$ -benzoinoxime in the analysis of copper in copper-molybdenum steels, which is simpler than methods previously used. This method gives excellent results and requires only 1 hour as compared to 3-6 hours necessary using older methods. It is also suitable for the analysis of all grades of steel where molybdenum and copper are present either as impurities or as alloying elements.

**Procedure.** Weigh accurately a 2 to 5 g. sample of the steel, depending on the copper content, and place in a 600-ml. beaker. The sample should contain from 0.1-0.3 g. of copper. Add 50-100 ml. of 10 per cent sulfuric acid and heat until solution is complete. If vanadium is absent, dilute the solution to 250 ml. with hot distilled water, and heat to boiling. For each gram of steel, add 1 g. of sodium thiosulfate dissolved in 10-50 ml. of water. Boil the solution 10-15 minutes and allow the precipitate to settle.

If vanadium is present, add a few crystals of potassium chlorate to the sulfuric acid solution and heat to dissolve the insoluble material. Dilute to 400 ml. with hot water. Saturate with hydrogen sulfide for 15 minutes and allow the precipitate to settle.

Filter, wash the precipitate with 1 per cent sulfuric acid, and transfer the filter and contents to a silica crucible, and ignite to a dull red heat. Cool, dissolve the precipitate in 10 ml. of hydrochloric acid with heating, and transfer this solution to a 400-ml. beaker. Add 3 drops of nitric acid and then an excess of ammonium hydroxide, and heat to boiling. Filter, wash with a hot ammoniacal solution, and combine the filtrate and washings in a 600-ml. beaker. Dilute to 250 ml. and heat to boiling, and slowly add 15 ml. of a 1 per cent alcoholic solution of  $\alpha$ -benzoinoxime with stirring. Boil for 1 minute, add a little ashless paper pulp and filter. Wash 5-6 times with a 3 per cent ammonium hydroxide solution, transfer to a silica crucible and ignite. Cool and weigh as CuO.

For the analysis of a tungsten steel proceed as follows:

**Procedure.** Dissolve a 2-5 g. accurately weighed sample in 50 ml. of hydrochloric acid with the aid of heat. Add 5 ml. of nitric acid, evaporate to dryness, cool and dissolve the iron, chromium and other elements which may be present in 25 ml. of hydrochloric acid with the aid of heat. Add a crystal of potassium chlorate and heat until the tungstic oxide is completely separated. Add 150 ml. of water, heat to boiling, cool, filter, and wash the precipitate with 5 per cent hydrochloric acid. To the filtrate and washings, add 10-25 g. of citric acid and make the solution alkaline with ammonium hydroxide. Acidify with hydrochloric acid and add an excess of 2 ml. of acid for each 100 ml. of the

solution. Heat to boiling and saturate with hydrogen sulfide. Filter, and proceed as described above.

The results obtained by Kar<sup>23</sup> in the analysis of a series of U. S. Bureau of Standard samples is given in Table 37.

TABLE 37.—ANALYSIS OF U. S. BUREAU OF STANDARD SAMPLES

Standard Sample	Average of Copper Reported Per Cent	Quantity of Copper Determined Using $\alpha$ -Benzoinoxime Per Cent
20c	0.255	0.263
30c	0.099	0.105
32b	0.117	0.13
33b	0.114	0.120
35a	0.267	0.27
72	0.064	0.07
73	0.033	0.04
101	0.055	0.064
106	0.142	0.16
111	0.122	0.135

To avoid the errors first pointed out by Azzalin<sup>17</sup> and Shik,<sup>18</sup> Silverman<sup>24</sup> has suggested separating copper by precipitating with  $\alpha$ -benzoinoxime, and then making the final determination of copper either by electro-deposition or by an iodide titration method.

The following procedure may be used for the determination of copper in ferromolybdenum, calcium molybdate and similar materials.

**Procedure.** If silicon is also to be determined, accurately weigh a 1-g. sample and place in a tall 300-ml. beaker. Treat with 20 ml. of 1:2 nitric acid, and allow the mixture to stand until rapid action has ceased. Heat the beaker until solution is almost complete, then cool somewhat, and add cautiously 10 ml. of concentrated sulfuric acid. Heat until heavy fumes of sulfuric acid appear, and then cool. Add 75 ml. of 1:4 hydrochloric acid, and heat until all soluble salts are dissolved, and then filter immediately. Wash alternately with cold 1:4 hydrochloric acid and water six times, and then wash with hot solutions to remove iron completely. Use the filtrate for the determination of copper.

If silicon is not to be determined, bring about the complete solution of the sample by the nitric acid mixture with the aid of hydrofluoric acid. Cool, dilute with water and add 10 ml. of hydrochloric acid.

In the analysis of molybdenum steels, solution of the sample in nitric acid may be followed by fuming with perchloric acid. Allow to cool and add water and hydrochloric acid.

For the analysis of calcium molybdate, use 25 ml. of 2:1 hydrochloric acid. For ferrotungsten, use 10 ml. of 1:4 nitric acid, 5 ml. of hydrochloric acid, and then add hydrofluoric acid dropwise until solution is complete.

Dilute the solution prepared as described above to about 150-200 ml., and add 15 g. of Rochelle salt dissolved in 15 ml. of water. Add a concentrated solution of sodium hydroxide until the mixture is alkaline to Congo red paper but is still acid to litmus paper. Cool, if necessary, to room temperature, and add ammonium hydroxide until the solution turns blue (if the copper content is about 0.5 per cent), or until the mixture is distinctly alkaline to litmus, and then add 5 ml. in excess. Add slowly with stirring a sufficient quantity of a 2 per cent solution of  $\alpha$ -benzoinoxime for complete precipitation. Ten ml. should be used for 0.0 to 0.5 per cent copper, and 15 ml. for 0.5 to 1.5 per cent copper. Allow the mixture to stand for 15 minutes, and filter through a 11-cm. No. 40 Whatman filter paper. Wash with a warm 1 per cent ammonium hydroxide solution.

Return the filter and contents to the beaker, and add 15 ml. of nitric acid (sp. gr. 1.4) and 10 ml. of 60-70 per cent perchloric acid. Mix well and heat until all nitric acid has been expelled and the perchloric acid condenses on the walls of the beaker. Cool, dilute with water, and boil to expel chlorine. The copper in this solution may be determined by the iodide titration.<sup>25-27</sup> or determined electrolytically as follows: Add ammonium hydroxide until the solution is blue, and then add nitric acid until the color is discharged. Add 4.0 ml. of 1:1 sulfuric acid and deposit the copper at 3 volts and 0.5 ampere.

Langer<sup>7</sup> has investigated the use of  $\alpha$ -benzoinoxime as a possible reagent for the amperometric titration of copper. The results obtained using this method are reported accurate to within about  $\pm 1$  per cent. Nickel interferes strongly with this determination. Copper may be determined in the presence of nickel by first precipitating the latter with dimethylglyoxime and precipitating copper in the filtrate with the aid of  $\alpha$ -benzoinoxime. The following microdetermination is described by Strebinger and Pollak:<sup>28</sup>

**Procedure.** Place 2-3 ml. of solution to be analyzed in a flask and add a few drops of ammonium hydroxide until the solution turns blue. Add a slight excess of 1 per cent alcoholic dimethylglyoxime and heat for 30 minutes at 70° C. Filter with the aid of a Pregl filter tube, and wash the precipitate 2-3 times with a little hot water. Carefully remove this filtrate and save for the copper determination. Continue to wash the precipitate to remove all soluble salts, first using hot 3 per cent ammonium hydroxide solution, and finally alcohol. Determine nickel in this precipitate. To the filtrate from the nickel precipitation, add 3-4 drops of 1 per cent alcoholic  $\alpha$ -benzoinoxime, and heat on a water bath for 30 minutes. Filter and wash with hot 3 per cent ammonia, and finally with 50 per cent alcohol. Complete the determination as described above.

$\alpha$ -Benzoinoxime has been used for the determination of copper in organic matter,<sup>29</sup> soil<sup>30</sup> and sea water.<sup>31</sup>

Yagoda<sup>32,33</sup> has used  $\alpha$ -benzoinoxime for the semi-quantitative estimation of copper by means of spot tests. The spot is formed on a reaction field of unit area, and the test is so carried out that the reaction product is uniformly distributed over it. By comparing the spot so formed with a series of standards, a close approximation of the copper content of the unknown may be determined.

Mironoff<sup>84</sup> and Ishibashi and Funahashi<sup>85</sup> have determined copper titrimetrically by the procedure of Tougarinoff.<sup>86</sup> The copper is precipitated in the usual manner, and after filtration the copper precipitate is hydrolyzed to a hydroxylamine salt by heating with sulfuric acid. An excess of ferric alum is then added and the ferrous salt so formed is determined manganometrically. The procedure used is essentially the same as that described in the section on dimethylglyoxime (page 197). The benzoin which is formed, however, must be removed to avoid high results.

**Detection and determination of molybdenum and tungsten.** Molybdenum is quantitatively precipitated from an acid solution by the addition of  $\alpha$ -benzoinoxime.<sup>37</sup> Precipitation is quantitative in acetic acid solutions buffered with acetate, and also occurs in cold mineral acid solutions containing as much as 20 per cent by volume of sulfuric acid. A true salt of molybdenum apparently is not formed, but only an addition compound of molybdic acid and the reagent, which is similar to the so-called heteropoly acids. Tungsten is similarly precipitated with  $\alpha$ -benzoinoxime, and the insoluble compound appears to be an addition compound of tungstic acid and  $\alpha$ -benzoinoxime.<sup>22</sup> The reaction between  $\alpha$ -benzoinoxime and molybdic acid has been used by Knowles<sup>37</sup> for the determination of molybdenum in the absence of tungsten, palladium, hexavalent chromium and pentavalent vanadium and tantalum. According to Knowles<sup>37</sup> the best conditions for the precipitation of molybdenum with  $\alpha$ -benzoinoxime are as follows:

**Procedure.** To the solution containing not more than 0.15 g. of molybdenum as  $\text{MoO}_3$ , add 10 ml. of concentrated sulfuric acid and dilute to 200 ml. Treat with sulfur dioxide to reduce any pentavalent vanadium and hexavalent chromium, and then boil until all excess sulfur dioxide is expelled. Cool the solution to 5-10° C., and add slowly with stirring 10 ml. of a 2 per cent alcoholic solution of  $\alpha$ -benzoinoxime, and add an additional 5 ml. for each 10 mg. of molybdenum present. Stir, and add sufficient bromine to impart a pale yellow color to the solution, and add an additional few ml. of the reagent. Allow the beaker and contents to remain in the cooling mixture for 10-15 minutes with occasional stirring, and stir into it a little macerated filter paper pulp. Filter through a close texture filter paper, such as S & S No. 589 Blue Band. Wash with 200 ml. of a cold freshly prepared mixture of 25-50 ml. of reagent, 10 ml. of concentrated sulfuric acid, and sufficient water to make 1 liter of solution. Transfer the washed precipitate to a weighed platinum crucible, char cautiously without flaming over a very low gas flame, and ignite to a constant weight in an electric muffle at 500-520° C. Weigh as  $\text{MoO}_3$ , which contains 66.67 per cent of molybdenum.

Isibasi<sup>16</sup> has studied the proper ignition temperature for converting the  $\alpha$ -benzoinoxime compound to  $\text{MoO}_3$ , and reports that the precipitates should be heated at 530-550° C.

Tungsten and palladium also appear to be quantitatively precipitated with  $\alpha$ -benzoinoxime. Selenium, tellurium, rhenium, ruthenium, rhodium, osmium, iridium and platinum are not precipitated alone with  $\alpha$ -benzoinoxime, but their

behavior in mixtures with molybdenum apparently has not been studied. Columbium and silicon contaminate the molybdenum precipitate, and must be removed prior to the determination. Silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, aluminum, iron, titanium, zirconium, trivalent chromium, tetravalent vanadium, cerium, uranium, nickel, cobalt, manganese and zinc are not precipitated with  $\alpha$ -benzoinoxime alone or when mixed with molybdenum. The results obtained by Knowles<sup>37</sup> in the determination of molybdenum in the presence of other metals is given in Table 38:

TABLE 38.—DETERMINATION OF MOLYBDENUM IN PRESENCE OF OTHER ELEMENTS

Mo Added g.	Mo Found g.	Difference g.	Precipitated in
0.0103	0.0101	—0.0002	5% HCl + 1% HNO <sub>3</sub>
0.0103	0.0102	—0.0001	5% HCl
0.0513	0.0532	+0.0009	Presence of 0.05 g. V <sup>+5</sup>
0.0513	0.0514	+0.0001	Presence of 0.05 g. V <sup>+5</sup>
0.0513	0.0514	+0.0001	Presence of 0.05 g. Sn <sup>+4</sup> in 5% HCl
0.0513	0.0514	+0.0001	Presence of 0.05 g. each Ni, Co, Mn, Cr, <sup>+3</sup> Fe, <sup>+3</sup> Zn, Cu
0.0513	0.0514	+0.0001	Presence of 0.05 g. each Ti, Zr, Ce <sup>+3</sup> , Al, U
0.0513	0.0510	—0.0003	Presence of 0.05 g. each Pb, As, Sb after removing Pb as PbSO <sub>4</sub>
0.0513	0.0516	+0.0003	Presence of 0.05 g. each of Ag, Bi, Cd, Hg <sup>+2</sup>
0.0513	0.0516	+0.0003	Presence of 0.05 g. Sb <sup>+5</sup> in 5% acid (50% HCl-50% H <sub>2</sub> SO <sub>4</sub> )

Knowles<sup>37</sup> describes the following method for the determination of molybdenum in steel:

**Procedure.** Dissolve 1 g. of steel in 50 ml. of 1:6 sulfuric acid, and treat with the smallest possible quantity of nitric acid to decompose any carbides and to oxidize molybdenum. Filter the solution if not perfectly clear, and dilute to 100 ml. Cool and treat with sufficient ferrous ammonium sulfate to reduce vanadic and chromic acids. Cool to 5-10° C., and add 5-10 ml. of a 2 per cent alcoholic solution of  $\alpha$ -benzoinoxime and then add bromine water until the solution is slightly yellow and a few ml. more of the reagent. Allow to stand for 10 minutes, and filter, wash and ignite as described above.

The above method may also be used for the determination of molybdenum in ores. The results obtained by this method are given in Table 39:

Yagoda and Fales<sup>38</sup> have used a similar method for the determination of molybdenum and tungsten in steel. Tungsten is precipitated under essentially the same conditions as used for molybdenum. The conditions recommended are to add 10 ml. of a 2 per cent alcoholic solution of the reagent to an acidified solution of tungsten containing 5 per cent of 12 M hydrochloric acid and cooled to 5-10° C.

TABLE 39.—DETERMINATION OF MOLYBDENUM IN STEEL

Material	Mo Added or Present %	Found %	Difference %	Remarks
Cr-Mo steel No. 72	0.149	0.166	+0.017	Gravimetric
Cr-Mo steel No. 72	0.149	0.160	+0.011	Gravimetric
B.O.H. steel No. 11d	0.0051	0.0054	+0.0003	Colorimetric after solution of precipitate
B.O.H. steel No. 11d	0.0103	0.0096	—0.0007	Colorimetric after solution of precipitate
B.O.H. steel No. 11d	0.51	0.52	+0.01	Gravimetric
B.O.H. steel No. 11d	5.13	5.15	+0.02	Gravimetric

This method has been used largely for concentrating molybdenum and tungsten as a unit, free from interfering elements. The results obtained in precipitating tungsten from pure solutions of sodium tungstate are given in Table 40.

TABLE 40.—PRECIPITATION OF TUNGSTEN WITH  $\alpha$ -BENZOINOXIME

Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O g.	Weight of WO <sub>3</sub>		Difference g.
	Found g.	Calculated g.	
0.0500	0.0348	0.0352	—0.0004
0.0250	0.0178	0.0176	+0.0002
0.0250	0.0170	0.0176	—0.0006
0.0100	0.0065	0.0070	—0.0005
0.0100	0.0067	0.0070	—0.0003

Taylor-Austin<sup>39</sup> has studied the various methods employed for the determination of molybdenum in cast iron, and reports that good results are obtained by weighing the molybdenum as lead molybdate after first removing iron with sodium hydroxide, by precipitating with  $\alpha$ -benzoinoxime and weighing as MoO<sub>3</sub>, or by precipitating with  $\alpha$ -benzoinoxime and eventually weighing as lead molybdate.

The following advantages of the  $\alpha$ -benzoinoxime method over the lead molybdate or molybdenum sulfide methods are:

(a) Samples weighing 3 g. or more may be conveniently used.

(b) The method provides for the complete separation in one operation of molybdenum from all elements commonly found in cast iron with the exception of silicon. Thus, nickel, titanium, phosphorus, manganese and iron do not precipitate under any conditions, while chromium and vanadium are not precipitated in the reduced state, and copper is not precipitated from an acid solution.

(c) In the lead molybdate method, a sodium hydroxide separation is necessary to remove iron, while vanadium, if present, requires special treatment.

In the sulfide method, molybdenum is still associated with other elements of the hydrogen sulfide group, such as arsenic and copper. The use of  $\alpha$ -benzoinoxime avoids many tedious separations.

For complete precipitation, Taylor-Austin<sup>39</sup> recommends about three times the theoretical quantity of  $\alpha$ -benzoinoxime as determined by the relationship, 1 atom Mo : 3 moles  $\alpha$ -benzoinoxime. Taylor-Austin<sup>39</sup> also recommends as a reagent a solution of  $\alpha$ -benzoinoxime in acetone.

Steele<sup>40</sup> reports the method of Taylor-Austin applicable to routine analyses of alloy cast iron and nickel-chromium-vanadium steel of the 18-8 type. Steele<sup>40</sup> found, however, that a stock solution of  $\alpha$ -benzoinoxime in alcohol showed no change after standing for four months, while the acetone solution recommended by Taylor-Austin deteriorated rapidly on standing for more than two weeks. For this reason, it appears that the alcohol solution of reagent is better suited for the preparation of stock solutions. Thompson and Stott<sup>41</sup> have also used  $\alpha$ -benzoinoxime for the estimation of molybdenum in cast iron.

Clarke<sup>42</sup> has described a method for the determination of molybdenum in steel, which is applicable to a wide range of steels, and is especially useful for the rapid determination of molybdenum in steels high in chromium and carbon, and which contain carbides that are practically insoluble in hydrochloric, nitric and sulfuric acids, or any combinations of these acids. Hot concentrated perchloric acid is used to decompose such carbides as those of chromium, molybdenum and vanadium. This eliminates the long and tedious fusions with sodium bisulfate and subsequent extractions of any molybdenum which may have been retained in the form of carbides. The method is quite accurate and requires approximately one hour for a complete analysis.

**Reagent.** Dissolve 2 g. of  $\alpha$ -benzoinoxime in 100 ml. of alcohol.

**Procedure.** Dissolve 1-2 g. of steel, depending upon the quantity of molybdenum present, in a mixture of 30 ml. of hydrochloric acid, 20 ml. of nitric acid and 25 ml. of 70 per cent perchloric acid. When the steel has dissolved, add about 2 ml. of hydrofluoric acid and evaporate until the mixture fumes strongly. Cool, add 100 ml. of water and heat until all chromic acid has passed into solution. Make the solution alkaline with ammonium hydroxide to dissolve any  $\text{MoO}_3$  which may have precipitated during the evaporation. Heat to boiling, and make the mixture about 5 per cent acid with sulfuric acid. Cool and add 50 ml. of a 6 per cent solution of ferrous sulfate, or a quantity sufficient to reduce chromium, vanadium and any other reducible substances that may be present. Cool to 10° C., and add bromine water until the solution has a slightly yellow color, and then add a solution of 2 g. of  $\alpha$ -benzoinoxime in 100 g. of alcohol. For the precipitation add 10 ml. of the reagent for the first 1 per cent of molybdenum present and 5 ml. for each additional per cent. Stir well, allow to stand for 10 minutes, and then filter through a 12-cm. ashless filter paper in a Buchner funnel. Wash the precipitate free of iron and other substances with a 1 per cent sulfuric acid solution containing a few ml. of the  $\alpha$ -benzoinoxime solution.

Remove the filter paper and precipitate from the funnel and transfer to a 600-ml. beaker. Add 25 ml. of perchloric acid and 15 ml. of nitric acid and



boil until the mixture fumes strongly. Cool, dilute with water to 200 ml., and add ammonium hydroxide until the mixture is faintly alkaline. Heat to boiling and filter off any iron that may be present, and wash the precipitate well with hot water. To the filtrate add sufficient hydrochloric acid to make the solution just acid, and then add 4 ml. in excess. Add 50 ml. of 50 per cent ammonium acetate solution and heat to boiling, and then add 20 ml. of a 4 per cent lead acetate solution. Boil for 3 minutes. Filter while hot, and wash the precipitate free of lead salts with hot water. Heat at a temperature not exceeding 500° C. and weigh as  $\text{PbMoO}_4$ . The molybdenum factor is 0.2613.

Make a blank determination and deduct the results from that obtained above.

Baker<sup>48</sup> has combined certain features of the method of Taylor-Austin<sup>89</sup> and Knowles<sup>37</sup> for the determination of molybdenum in cast iron and steel respectively, and proposes the following procedure:

**Procedure.** Place 3 g. of steel containing 0.2-0.3 per cent molybdenum (or a suitable equivalent of steel having a different composition) in a 250-ml. beaker, and add 25-30 ml. of 68-70 per cent perchloric acid. Cover with a watch glass and heat carefully to bring about solution of the sample. Allow the solution to boil lightly for 10-15 minutes, and remove from the hot plate and allow to cool. Add carefully 100 ml. of distilled water and heat to boiling, and filter on a Whatman No. 31 or similar grade paper into a 600-ml. beaker. Wash the filter and the precipitate once with hot water and heat the filtrate on the hot plate. When the filtrate is boiling, add 15 ml. of sulfurous acid and continue to boil to remove the excess sulfur dioxide. Cool the mixture to 5-10° C. in an ice-bath, and by the addition of ice. The total volume of the solution should be 200-300 ml. Add 10 ml. of a solution prepared by adding 2 g. of  $\alpha$ -benzoinoxime to 100 ml. of acetone, and add sufficient bromine water to color the solution a pale yellow. Add an additional 5 ml. of the  $\alpha$ -benzoinoxime solution. Stir at intervals over a period of 10 minutes, and filter through a Whatman No. 31 or similar grade paper.

Wash the precipitate with a cold solution prepared from 25-50 ml. of the  $\alpha$ -benzoinoxime solution, 1 liter of distilled water and 10 ml. of sulfuric acid. Char, but do not burn over a gas flame or hot plate, and ignite the precipitate at 500-525° C. Weigh as  $\text{MoO}_3$ .

Carlsson<sup>44</sup> has used  $\alpha$ -benzoinoxime for the determination of small quantities of molybdenum in ores. Lelubre<sup>45</sup> objects to the use of  $\alpha$ -benzoinoxime for the precipitation of molybdenum, since this procedure involves what he considers an unnecessary expense. He recommends the precipitation of the molybdenum as lead molybdate or as molybdenum sulfide.

**Detection of basicity.** Feigl and da Silva<sup>46</sup> have recommended the use of dimethylglyoxime,  $\alpha$ -benzoinoxime and thionalide for the preparation of reagents which can be used for the detection of basicity in slightly soluble materials such as aluminum oxide, barium carbonate, calcium phosphate, etc. For the details of this procedure see section on dimethylglyoxime.

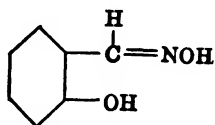
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44. C. G. Carlsson, *Jernkontorets Ann.* **125**, 697-704 (1941); *C.A.* **37**, 5672 (1943).
45. R. Lelubre, *Ing. chim.* **25**, 101-17, 121-38 (1941); *C.A.* **37**, 5672 (1943).
46. F. Feigl and C. P. J. da Silva, *Ind. Eng. Chem., Anal. Ed.* **14**, 316-19 (1942); *C.A.* **36**, 3454 (1942).
47. J. V. Dubsky, *Mikrochemie*, **23**, 42-50 (1937).
48. F. Pavelka and G. Setta, *Mikrochem. ver. Mikrochim. Acta* **31**, 73-82 (1943); *C.A.* **38**, 1974 (1944).

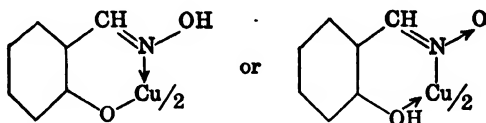
## CHAPTER VIII

### HYDROXYOXIMES

A number of oximes containing the group



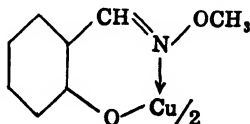
form bright yellowish to greenish copper salts which are insoluble in dilute acetic acid. Best known of this class is salicylaldoxime,  $\text{HO}-\text{C}_6\text{H}_4-\text{CH}=\text{NOH}$ , which was first employed by Ephraim<sup>1</sup> for the detection and gravimetric determination of copper. In the formation of the copper salt, salicylaldoxime acts as a monobasic acid in which the hydrogen atom of either the acidic phenolic group or the oxime group may be replaced by an equivalent of the metal. The copper atom in turn is coordinated to the other group to form typical inner-complex compounds.



Ephraim assumed that it is the phenolic hydrogen atom which is replaced, and this view has been supported by the investigations of Feigl and Bondi<sup>2</sup> on the reactions of the isomeric methyl ethers of salicylaldoxime.



The compound containing the free hydroxyl group reacts with cupric acetate



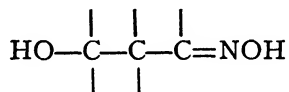
to form a dark brown salt, while the isomeric phenolic ether does not react.

Ephraim<sup>3</sup> has studied the reactions of a number of compounds which contain the same reactive grouping as salicylaldoxime, and has found that all form yellowish copper salts which are only slightly soluble in acetic acid. These compounds are

1-Acetyl-2-hydroxynaphthoic acid-3-oxime  
 1-Acetyl-2-naphtholoxime  
 Gallacetophenoneoxime  
*o*-Hydroxyacetophenoneoxime  
*o*-Hydroxybenzophenoneoxime  
 1-Naphthol-2-aldoxime  
 2-Naphthol-1-aldoxime  
 Paeonoloxime  
 Quinacetophenoneoxime  
 Quinacetophenonemethyletheroxime  
 Resacetophenoneoxime  
*o*-Vanillinoloxime

None of these seems to offer any special advantage over the more readily available salicylaldoxime, but their reactions illustrate the selective or specific action of certain atomic groupings. The specific action of these compounds, however, appears only in acetic acid solutions. Many other metals are precipitated by salicylaldoxime in neutral or slightly alkaline solutions,<sup>4</sup> but only the palladium salt is obtained in dilute mineral acid solutions.

The group



which is contained in salicylaldoxime and other *o*-hydroxyaloximes is not in itself sufficient to yield a specific copper reaction. Pentanol-2-one-4-oxime,  $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{C}(=\text{NOH})-\text{CH}_3$ , and chloral acetophenone oxime,  $\text{CCl}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{C}(=\text{NOH})-\text{C}_6\text{H}_5$ , which contain the same grouping, do not yield insoluble copper salts nor color reactions which would indicate the formation of copper salts. From this fact it must be concluded that differences in steric configuration and in the enhanced acidity of the hydroxyl group because of its linkage to the aromatic ring are responsible for the copper specific action of the group  $\text{HO}-\text{C}_6\text{H}_4-\text{C}(=\text{NOH})-$ .

1. F. Ephraim, *Ber.* **63**, 1928 (1930).
2. F. Feigl and A. Bondi, *Ber.* **64**, 2819 (1931).
3. F. Ephraim, *Ber.* **64**, 1210 (1931).
4. H. Holzer, *Z. anal. Chem.* **95**, 392 (1933).

## 5-CHLOROSALICYLALDOXIME

$\text{C}_7\text{H}_6\text{O}_2\text{NCl}$

Mol. Wt. 171.58

Beil. Ref. VIII, 53.



**Use:** Detection of bismuth, copper, iron, lead and nickel.

5-Chlorosalicylaldoxime is obtained as a crystalline solid from alcohol. It melts at 123-124° C.

**Preparation. 5-Chlorosalicylaldehyde:** Place 20 g. of salicylaldehyde in a flask, and while warming on a water bath, pass a stream of chlorine slowly through the mixture for about 1 hour. The mixture becomes light green and finally bright yellow, and on cooling the mixture solidifies. Add 30 g. of alcohol and warm slightly. Allow to cool and collect the crystals which separate.<sup>1</sup>

**5-Chlorosalicylaldoxime:** Mix an alcoholic solution of 5-chlorosalicylaldehyde with an aqueous solution of an equivalent quantity of hydroxylamine hydrochloride and sodium carbonate, and clear the mixture with a little alcohol. Allow to stand for 24 hours, and acidify slightly with hydrochloric acid. Evaporate to dryness. Extract the residue with absolute alcohol, and precipitate 5-chlorosalicylaldoxime by diluting the alcoholic extract with water.<sup>2</sup>

**Reactions with cations.** Flagg and Furman<sup>8</sup> have studied the effect of introducing a chlorine atom into the salicylaldoxime molecule upon the analytical characteristics of the latter reagent, and they have found that its properties are not altered to any marked extent. 5-Chlorosalicylaldoxime reacts with a number of cations to give color reactions or precipitates which might be used for analytical purposes, but the use of this reagent offers no advantages over the simpler and more readily available salicylaldoxime. The blue color given by 5-chlorosalicylaldoxime and the ferric ion is of exceptional interest.

The reactions with 5-chlorosalicylaldoxime and various ions are carried out as follows:

**Reagent.** Dissolve 0.5 g. of 5-chlorosalicylaldoxime in 25 ml. of alcohol and dilute with water to 100 ml.

TABLE 41.

Substance Tested	Results
Ag <sup>+</sup>	Yellow-white precipitate
Pb <sup>++</sup>	Yellow precipitate
Hg <sup>++</sup>	White precipitate
Cu <sup>++</sup>	Light brown precipitate
Cd <sup>++</sup>	Pale yellow precipitate
Bi <sup>+++</sup>	Bright yellow precipitate
Mn <sup>++</sup>	Green-brown precipitate
Fe <sup>++</sup>	Green-brown precipitate
Fe <sup>+++</sup>	Blue color
Co <sup>++</sup>	Brown precipitate
Ni <sup>++</sup>	Green precipitate
Zn <sup>++</sup>	Light yellow precipitate
Pd <sup>++</sup>	Yellow precipitate
OsO <sub>4</sub>	Orange color
Mg <sup>++</sup>	Light yellow precipitate
VO <sub>3</sub> <sup>-</sup>	Black precipitate
UO <sub>3</sub> <sup>++</sup>	Orange color
Ce <sup>++++</sup>	Light brown precipitate
Au <sup>+++</sup>	Brown precipitate

**Procedure.** Add 1 ml. of the reagent to 10 ml. of the solution to be tested. Various ions are indicated by color reactions or precipitates. These are listed in

Table 41. The reaction may be carried out on a spot plate by adding to 0.05 ml. of the solution to be tested 1 or 2 drops of a 1 per cent solution of 5-chlorosalicylaldoxime with sufficient alcohol to keep the oxime in solution.

The sensitivity of the 5-chlorosalicylaldoxime reactions with copper, lead, nickel and bismuth is somewhat less than those with salicylaldoxime and 5-nitrosalicylaldoxime (Table 42).

TABLE 42.—SENSITIVITY LIMITS OF DETECTION OF COPPER, LEAD, NICKEL, AND BISMUTH

(Expressed in parts of cation per number of ml. of solution)

Cation	Salicylaldoxime	5-Chlorosalicylaldoxime	5-Nitrosalicylaldoxime
Cu <sup>++</sup>	1:2,000,000	1:500,000	1:2,000,000
Pb <sup>++</sup>	1:50,000	1:10,000	1:50,000
Ni <sup>++</sup>	1:3,000,000	1:1,000,000	1:3,000,000
Bi <sup>+++</sup>	1:250,000	1:100,000	1:100,000

1. H. Biltz and K. Stepf, *Ber.* 37, 4024 (1904).
2. H. L. Visser, *Archiv der pharmazie*, 235, 548 (1897).
3. J. F. Flagg and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.* 12, 529-31 (1940); *C.A.* 34, 7204 (1940).

### 3,5-DIBROMOSALICYLALDOXIME

Flagg and Furman<sup>1</sup> have prepared the 3,5-dibromosalicylaldoxime, and have studied its use in analytical procedures, but because of the relative insolubility of this compound, it has been proved to be of practically no value as an analytical reagent. A solution can be prepared by dissolving 1 g. of the oxime in 75 ml. of alcohol and diluting to 100 ml., but when this solution is added to aqueous solutions containing ions to be tested, reactions of possible analytical value are usually obscured by precipitation of the reagent.

1. J. F. Flagg and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.* 12, 529-31 (1940); *C.A.* 34, 7204 (1940).

### *p*-HOMOSALICYLALDOXIME

Synonym: *p*-Methylsalicylaldoxime, 3-methyl-6-hydroxybenzaloxime

C<sub>8</sub>H<sub>9</sub>O<sub>2</sub>N

Mol. Wt. 151.15

Beil. Ref. VIII, 100.



**Use:** Determination of copper.

*p*-Homosalicylaldoxime is obtained as colorless needles from water. It melts at 105° C. It is slightly soluble in cold water, easily soluble in alcohol, ether, chloroform, benzene, and hot water.

**Preparation:** Treat 10 g. of *p*-homosalicylaldehyde with 200 ml. of 3 N sodium hydroxide and 7 g. of hydroxylamine hydrochloride and warm.<sup>1,2</sup>

**Determination of copper.** Copper is precipitated quantitatively with *p*-homosalicylaldoxime.<sup>2</sup>

**Procedure.** To 5 ml. of the copper solution, add 10 ml. glacial acetic acid, 100 ml. of water, and 1 g. of sodium acetate. Heat to 80° C. and add 25 ml. of a 1 per cent solution of the reagent. Allow to stand 2-3 hours and filter through a Gooch crucible. The factor for copper is 0.1748.

A similar precipitate is obtained with nickel.

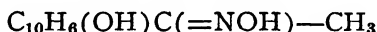
1. O. Goldbeck, *Ber.* **24**, 3658 (1891).

2. Chung-Hsi Kao and Kuang-Hsu Chen, *J. Chinese Chem. Soc.* **3**, 22-6 (1935); *C.A.* **29**, 4691 (1935).

## 2-HYDROXY-1-ACETONAPHTHONEOXIME

$C_{12}H_{11}O_2N$

Mol. Wt. 201.21



**Use:** Detection of cobalt, copper, nickel and zinc.

This reagent is obtained as leaves which melt at 86° C.

**Preparation:** Dissolve 1.86 g. of 1-aceto-2-naphthol and 1.4 g. of hydroxylamine hydrochloride in 40 ml. of 70 per cent alcohol. Add 5 g. of crystalline sodium acetate and boil for 90 minutes under reflux. Filter off the sodium chloride which forms with suction, and add water to the filtrate as long as any precipitate forms. The oil crystallizes by rubbing.

**Detection of copper.** 2-Hydroxy-1-acetonaphthoneoxime reacts like salicylaldoxime toward copper, but possesses the advantage over the latter compound in that the copper salt is more highly colored and is more easily discernible. When the reagent is added to a moderately concentrated solution of a copper salt, a violet-brown color appears, but at greater dilution the color is rose-violet. The copper salt of the reagent is less soluble than the corresponding salts of other metals. Nickel, cobalt, zinc, and cadmium salts are soluble in acetic acid, or partially so, while the copper salt is insoluble.

In neutral solutions, nickel, cobalt, and zinc salts give, according to dilution, no precipitation, or only a slight turbidity. A yellowish-green nickel salt is obtained on the addition of sodium acetate. Similarly, a weak, yellowish-brown color is obtained with cobalt, and a white precipitate is obtained with zinc. Cadmium yields no precipitate. Ferric salts yield a dark green color, which on the addition of sodium acetate turns to a deep violet-brown.

The copper test may be carried out as follows:

**Reagent.** Dissolve one gram of the reagent in 5 ml. of alcohol, and pour this solution dropwise into 95 ml. of water previously heated to 80° C. Shake slightly, and filter when clear.

**Procedure.** Carefully neutralize the solution to be tested with acetic acid, and then add a few drops of the reagent. A violet-brown or rose-violet coloration forms, depending upon the concentration of copper.

1. F. Ephraim, *Ber.* **64B**, 1210-5 (1931); *C.A.* **25**, 3589-90 (1931).

### 5-NITROSALICYLALDOXIME



Mol. Wt. 182.12



**Use:** Detection of bismuth, copper, lead and nickel.

5-Nitrosalicylaldoxime is obtained as a crystalline solid which melts at 220-223° C. with some decomposition.

**Preparation.** *5-Nitrosalicylaldehyde:* Pour slowly, with cooling in ice, 1.5 parts of fuming nitric acid into a mixture of 1 part salicylaldehyde and 5 parts of glacial acetic acid so that the temperature does not rise above 15° C. When all the acid has been added, warm the mixture to 40-45° C. and pour quickly into ice water. Dissolve 100 parts of the precipitate with warming in 270 parts of water and 25 parts of sodium hydroxide, and allow to stand 12 hours. Dissolve the crystallized sodium salt in the smallest possible quantity of hot water and allow to cool. The crystals of the sodium salt which separate may be converted into 5-nitrosalicylaldehyde by acidifying with hydrochloric acid.<sup>1</sup>

TABLE 43.—REACTIONS WITH 5-NITROSALICYLALDOXIME

Ion Tested	Results
Ag <sup>+</sup>	Red precipitate
Pb <sup>++</sup>	Orange precipitate
Hg <sup>++</sup>	Light yellow precipitate
Cu <sup>++</sup>	Green-yellow precipitate
Cd <sup>++</sup>	Pale yellow precipitate
Bi <sup>+++</sup>	Orange precipitate
Mn <sup>++</sup>	Green-brown precipitate
Fe <sup>++</sup>	Green-brown precipitate
Fe <sup>+++</sup>	Violet color
Co <sup>++</sup>	Green precipitate
Ni <sup>++</sup>	Brownish-yellow precipitate
Zn <sup>++</sup>	Yellow precipitate
Pd <sup>++</sup>	Yellow precipitate
OsO <sub>4</sub>	Orange color
Mg <sup>++</sup>	Yellow precipitate
VO <sub>3</sub> <sup>-</sup>	Black precipitate
UO <sub>3</sub> <sup>++</sup>	Orange color
Ce <sup>++++</sup>	Red-brown precipitate
Au <sup>+++</sup>	Yellow precipitate

*5-Nitrosalicylaldoxime:* Dissolve 2 g. of the aldehyde in 25 ml. of alcohol and add a solution prepared by dissolving 0.82 g. of hydroxylamine hydrochloride



in a little water. Filter the heavy white precipitate which forms, wash well, and dry.<sup>2</sup>

**Reactions.** Flagg and Furman<sup>2</sup> have studied the effect of introducing a nitro group into the salicylaldoxime molecule, and they have found that the resulting derivative offers no advantages as an analytical reagent over the more easily prepared salicylaldoxime. The colors of certain derivatives of the 5-nitro-oxime, however, are more vivid than the colors of the corresponding compounds with salicylaldoxime. For example, the silver salt is red instead of yellowish-white, and is therefore more easily distinguishable.

The reagent is prepared by dissolving 0.25 g. of 5-nitrosalicylaldoxime in 60 ml. of alcohol and diluting with water to 100 ml. The tests are carried out by adding this reagent to nearly neutral solutions of ions to be tested. The results of these reactions are given in Table 43.

Salicylaldoxime and 5-nitrosalicylaldoxime are of about equal sensitivity for the detection of copper, lead and nickel, but the former is the more sensitive reagent for the detection of bismuth.

1. W. v. Miller, *Ber.* 20, 2109 (1887).

2. J. F. Flagg and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.* 12, 529-31 (1940); *C.A.* 34, 7204 (1940).

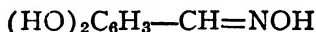
## RESORCYLALDOXIME

Synonym: 2,4-Dihydroxybenzaloxime

$C_7H_7O_3N$

Mol. Wt. 153.13

Beil. Ref. VIII, 243.



**Use:** Detection and determination of iron.

Resorcyaldoxime is a white crystalline solid melting at 198-199° C. It is soluble in alcohol and in ether.

**Preparation.** *Resorcyaldehyde:* Heat 200 g. of potassium ferrocyanide in a flask with a mixture of 160 g. of concentrated sulfuric acid and 280 ml. of water. Fit the flask with an air condenser, from the upper end of which hydrogen cyanide is conducted, first through an empty wash bottle, then through 3 calcium chloride towers, and finally into a flask kept at -5° C., and containing 1 part of resorcinol dissolved in 3 parts of anhydrous ether. Pass the gas into the solution until the increase in weight indicates a 50 per cent excess of hydrogen cyanide. Fit the flask with an outlet tube, which is passed into the draft flue of a hood. Use rubber stoppers.

Now add hydrogen chloride gas through the same drying train until no longer absorbed by the ether solution. Allow the mixture to stand several hours, and decompose by the addition of boiling water. Keep the temperature of the drying train at 35-40° C. by placing in a water bath. Filter the ether solution, and collect the crystals which separate on cooling.<sup>1,2</sup>

*Resorcyaldoxime:* The oxime is prepared by the reaction of the aldehyde and hydroxylamine hydrochloride in the presence of sodium carbonate and in a water-alcohol solution.<sup>3,4</sup> The compound is purified by recrystallizing from hot water.

**Detection and determination of iron.** A purple color is obtained when a slightly acid solution of ferric iron is treated with resorcyldoxime. This reaction is sensitive to 0.3 p.p.m. of iron and may be used for the detection and colorimetric determination of ferric iron.<sup>5</sup>

**Procedure.** Treat the slightly acidified unknown solution with 1 ml. of a 0.2 per cent solution of resorcyldoxime in a 50-ml. Nessler tube, and compare the purple color with that of standards similarly prepared. The color does not fade for six hours.

The reagent gives no color reaction with ferrous iron. Nickel, aluminum, chromium and cobalt do not interfere.

1. F. Tiemann and L. Lewy, *Ber.* 10, 2212 (1877).
2. T. B. Johnson and F. W. Lane, *J. Am. Chem. Soc.* 43, 355 (1921).
3. E. Marcus, *Dissertation*, Berlin (1890).
4. E. Marcus, *Ber.* 24, 3651 (1891).
5. S-L. Chien and T-M Shih, *J. Chinese Chem. Soc.* 5, 154-61 (1937); *C.A.* 31, 6130 (1937).

## SALICYLDALDOXIME

$C_7H_7O_2N$

Mol. Wt. 137.13

Beil. Ref. VIII, 49.



**Use:** Detection of copper, iron and vanadium.

Determination of bismuth, cadmium, copper, iron, lead, nickel, palladium and zinc.

Salicyldoxime is a white crystalline solid which melts at 57° C. It is only slightly soluble in water but dissolves readily in alcohol, ether, benzene and dilute hydrochloric acid. It also dissolves in water containing some ethyl alcohol. It is insoluble in petroleum benzene.

**Preparation:** Dissolve 12.9 g. of salicylaldehyde in 110 ml. of 2 N sodium hydroxide and add 6.2 g. of hydroxylamine hydrochloride. Warm the mixture for 30 minutes on a water-bath and acidify with acetic acid. Upon cooling the mixture with ice, salicyldoxime separates as an oil. Purify by recrystallizing first from benzene and then from petroleum ether containing a little benzene.<sup>1,2,3</sup>

**Reactions of salicyldoxime.** Salicyldoxime was originally proposed by Ephraim<sup>4,5</sup> as a reagent for the gravimetric determination of copper, and later other papers appeared describing the use of the reagent for the separation of copper from other elements. Salicyldoxime has more recently been found useful for the determination of lead,<sup>30,35</sup> palladium,<sup>6,7</sup> iron,<sup>4,33</sup> nickel,<sup>8</sup> bismuth,<sup>9,10</sup> and vanadium.<sup>9,10</sup> Flagg and Furman<sup>10</sup> have made a detailed study of the reactions of many ions with salicyldoxime, and have found that positive reactions are obtained with many substances. Their results are shown in Table 44.

TABLE 44.—REACTIONS OF SALICYLALDOXIME

Ion Tested	Result
Ag <sup>+</sup>	Yellow-white precipitate
Pb <sup>++</sup>	Yellow precipitate
Hg <sup>++</sup>	Light-yellow precipitate
Cu <sup>++</sup>	Greenish-yellow precipitate
Cd <sup>++</sup>	Pale yellow precipitate
Bi <sup>+++</sup>	Bright yellow precipitate
Mn <sup>++</sup>	Green-brown precipitate
Fe <sup>++</sup>	Brown precipitate
Fe <sup>+++</sup>	Red color
Co <sup>++</sup>	Brown precipitate
Ni <sup>++</sup>	Green precipitate
Zn <sup>++</sup>	Light yellow precipitate
Pd <sup>++</sup>	Yellow precipitate
OsO <sub>4</sub>	Orange-color or precipitate
Mg <sup>++</sup>	Light yellow precipitate
VO <sub>4</sub> <sup>-</sup>	Black precipitate
UO <sub>2</sub> <sup>++</sup>	Orange color
Ce <sup>++++</sup>	Brown precipitate
Au <sup>+++</sup>	Brown precipitate

Solutions of ceric salts and dichromates yield brown precipitates with the reagent, which appear to be oxidation products of the oxime. Holzer<sup>6</sup> reports that auric salts yield a brown-violet precipitate, which eventually turns dark-blue. Osmium tetroxide gives an orange color with the reagent, but only in an alkaline solution. Gahide<sup>7</sup> claims that under these conditions an orange precipitate is formed. Uranyl salts also give an orange color in an alkaline solution of the reagent.

The following ions give no positive reaction with salicylaldoxime in a neutral, slightly acid or ammoniacal solution. (It should be noted that solutions of some of the following ions cannot be prepared at certain pH ranges.) Lithium, sodium, potassium, rubidium, cesium, beryllium, calcium, strontium, barium, boron, aluminum, scandium, yttrium, lanthanum, trivalent cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, thulium, ytterbium, gallium, indium, trivalent thallium, titanium, zirconium, hafnium, thorium, germanate, tin, vanadyl, columbium, tantalum, arsenic, antimony, trivalent chromium, molybdate, tungstate, selenate, tellurate, permanganate, perhennate, iridium, platinum, trivalent ruthenium, and trivalent rhodium.

A number of metals, such as copper, lead, palladium, nickel and bismuth are quantitatively precipitated with salicylaldoxime.

Flagg and Furman<sup>10</sup> have studied the precipitation of various ions with salicylaldoxime, and have reported their results in Table 45, which is taken directly from their publication.\*

Jean<sup>11</sup> has recently studied the effect of pH upon the precipitation of metals with salicylaldoxime. He reports that cobalt and most of the nickel is precipi-

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tated at pH 7-8; lead at 8.9 or higher; bismuth at 3.4-7 and 9-10; zinc at 6.2-8; and palladium over a wide pH range. Vanadium is partially precipitated in 0.02-2.0 N sulfuric acid.

TABLE 45.—IONS WHICH YIELD PRECIPITATES WITH SALICYLALDOXIME

Ion	Color of Precipitate	pH of Initial Turbidity	Remarks
Ag <sup>+</sup>	Yellowish white	6.3	Soluble in acetic acid and in ammonia at pH 7.5 to 8.0.
Pb <sup>++</sup>	Yellow	5.0	Soluble in excess NaOH.
Hg <sup>++</sup>	Light yellow	5.3	Insoluble in excess NaOH.
Cu <sup>++</sup>	Greenish yellow	Acid solution	Complete above pH 2.6.
Cd <sup>++</sup>	Pale yellow	About 7	Gelatinous. Soluble in excess ammonia.
Bi <sup>+++</sup>	Bright yellow	6.7-7.0	Stable to at least pH 9.4 and probably beyond. Insoluble in excess ammonia.
Mn <sup>++</sup>	Green to brown	8.8-8.9	Soluble in large excess NaOH or ammonia.
Fe <sup>++</sup>	Brown	6.8-7.0	Soluble in excess alkali.
Co <sup>++</sup>	Brown	5.3-5.6	Dissolves at about pH 9.4.
Ni <sup>++</sup>	Green	3.3	Complete from pH 7 to 9.9. Soluble in concentrated NH <sub>4</sub> OH.
Zn <sup>++</sup>	Light yellow	6.2-6.5	Dissolves in ammonia at pH 8.8. to 9.4.
Pd <sup>++</sup>	Yellow	Acid solution	Reported to be quantitative in solutions containing free sulfuric acid.
Mg <sup>++</sup>	Light yellow	Slightly ammoniacal	Not quantitative.
VO <sub>5</sub> <sup>-</sup>	Black	Acid solution	Best range 0.05-1.0 N, but at most 60 to 70 per cent of vanadium is precipitated.

**Detection and determination of copper.** Salicylaldoxime reacts with copper in an acetic acid solution to form a yellowish-green precipitate of the copper salicylaldoximate.<sup>4,5,11-13,15</sup> This compound is usually formed with the replacement of the hydrogen atom of the hydroxyl group to form an inner-complex compound (page 252).

Under special conditions, however, a copper compound can be obtained in which both the hydroxyl and oxime hydrogen atoms have been replaced by the metal.

The formation of the green precipitate is sufficiently sensitive to make the reaction useful for the detection of small quantities of copper.

**Reagent.** Dissolve 1 g. of salicylaldoxime in 5 ml. of alcohol and pour this solution dropwise into 95 ml. of water which has been heated to 80° C. Shake slightly, and filter when clear.

When this reagent is to be used for the quantitative determination of copper, it is important that the temperature not be allowed to exceed 80° C. Otherwise, decomposition products are formed which are difficult to remove from the precipitate by washing, and which, if allowed to remain, cause considerable decomposition during subsequent drying.

Astin and Riley<sup>3</sup> recommend the following method for preparing a suitable salicylaldoxime reagent from salicylaldehyde.

**Reagent.** Dissolve 8.88 g. of salicylaldehyde in 32 ml. of ethyl alcohol, and add this solution to 5.08 g. of hydroxylamine hydrochloride dissolved in 8 ml. of water. Add 60 ml. of ethyl alcohol, and pour the resulting solution into 900 ml. of water that has been heated to 80° C. Stir well, cool, and filter.

**Procedure.** Carefully neutralize the solution to be tested, and make slightly acid with dilute acetic acid. Then add a few drops of the reagent to the cold solution. A greenish-yellow precipitate or opalescence forms, depending upon the amount of copper present. A distinct opalescence is observed if the solution contains 1 part of copper in 1,000,000 parts of water. The test is sensitive to 0.5γ of copper.

Mennucci<sup>36</sup> says that this method is capable of detecting 0.1-1.0γ of copper in 0.03-0.5 ml. of solution.

Many metallic ions yield precipitates with salicylaldoxime, but only in neutral or alkaline solutions. Palladium salts give a precipitate of  $\text{Pd}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ , and gold salts precipitate metallic gold when added to acetic acid solutions of the reagent. The only other substance to form a precipitate with the reagent in an acid solution is the vanadate ion. Pavelka and Setta<sup>37</sup> have used salicylaldoxime for the detection of copper as an impurity in samples of ammonium molybdate.

Copper is quantitatively precipitated from an acetic acid solution by the addition of an excess of salicylaldoxime, and this reaction has been used for the gravimetric determination of copper.<sup>1,3,5,8,14-16</sup> Copper is precipitated under the same conditions as outlined in the test for copper, except that an excess of the reagent is used to insure complete precipitation. The precipitate is washed with cold water until a portion of the filtrate gives no color reaction with ferric chloride. The precipitate is then dried at 100-115° C. and weighed as the oximate. This compound contains 18.95 per cent copper. The following procedure is recommended by Reif:<sup>15</sup>

**Procedure.** To 2-5 ml. of copper solution containing 0.4-3.5 mg. of copper, add ammonium hydroxide dropwise to the appearance of a blue color. Decolorize with a normal solution of ammonium acetate, and then add an excess of the freshly prepared alcoholic solution of the reagent. Filter, wash with water, and then with alcohol, and finally dry at 105-110° C. and weigh. If iron is present add a little tartaric acid. The factor for copper is 0.1895.

Hecht and Reissner<sup>11</sup> use the following procedure for the microdetermination of copper:

**Procedure.** Evaporate the solution to dryness, and dissolve the residue in 3 drops (1 drop = 0.025 ml.) of 6.5 per cent nitric acid. Transfer to a filter beaker. To the solution so obtained, which should not have a volume greater than 3 ml., add 1-2 per cent sodium hydroxide dropwise to the formation of a permanent turbidity, and then add 1:4 acetic acid until the turbidity just disappears. Now add a small excess of the salicylaldoxime reagent, and shake to coagulate the precipitate. Allow to stand 5-10 minutes and filter. Wash the precipitate with cold water until the filtrate no longer gives a violet color

with ferric chloride. Dry at 105-110° C. and weigh as copper salicylaldoximate. The factor for copper is 0.1895.

Only palladium and gold salts, and vanadates yield precipitates when treated with salicylaldoxime in an acetic acid solution; other metallic ions give precipitates only in neutral or alkaline solutions. Nickel may interfere with the copper determination, but may be removed by precipitating with dimethylglyoxime.<sup>15</sup>

A recent systematic study of the use of salicylaldoxime by Shik<sup>17</sup> has shown that by the use of a proper procedure, copper may be determined in the presence of iron, manganese, cobalt, nickel, zinc and cadmium. The determination of copper in acetic acid solution and in the presence of silver, however, is not accurate.

Finkel'shtein<sup>18</sup> and Alten and co-workers<sup>19</sup> have made the copper-salicylaldoxime reaction the basis for a nephelometric method for determining copper.

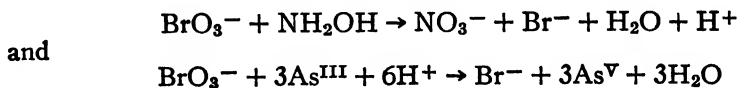
**Reagent.** Dissolve 1 g. of salicylaldoxime in 5 ml. of hot alcohol, and pour the hot solution into 95 ml. of water at 80° C. Shake well and filter.

**Procedure.** Neutralize with ammonia both the solution to be tested and a standard of known copper content. The solution and standard should be contained in 30- or 15-ml. graduated cylinders, depending upon the copper content. To each, add 3 ml. of glacial acetic acid, 1 ml. of 20 per cent potassium citrate, 2 ml. of saturated disodium phosphate solution and 0.5 ml. of saturated sodium acetate. Dilute to 22 or 12 ml., mix with a stirrer and place in a water-bath of definite temperature. Add 1 ml. of the salicylaldoxime solution and stir without scratching the sides of the cylinder. Allow to stand 1.5 hours with 0.03-0.1 mg. of copper, or 2.5 hours if 0.01-0.03 mg. of copper is present. Then add 1 ml. of glacial acetic acid and measure the turbidity.

Neuberger<sup>20,21</sup> has devised a method for the titration of copper with salicylaldoxime, with a polarimetric indication of the end-point.

Tougarinoff<sup>22</sup> has developed an indirect titrimetric method for determining copper, using salicylaldoxime. In this method the copper salicylaldoximate is decomposed by heating with an excess of a ferric salt in an acid solution, and the resulting salicylaldehyde is volatilized and the hydroxylamine is oxidized to nitrous oxide. The equivalent quantity of ferrous iron which is formed in the reaction with the oxime is determined by titration with a standard permanganate solution. This method is similar to that used for the determination of nickel with dimethylglyoxime (page 197).

Furman and Flagg<sup>23</sup> have proposed a bromate-arsenite method, which in some respects appears to be more satisfactory than that used by Tougarinoff.<sup>22</sup> The reactions upon which this determination is based are given by the following equations:



The bromate oxidizes hydroxylamine to the nitrate instead of nitrous oxide, as with ferric iron, and consequently there is a more favorable ratio of standard solution used per weight of metal. One gram atom of copper requires 14 equiva-

lents of the standard bromate solution. Copper is precipitated in the usual manner from a solution containing acetic acid and sodium acetate at a pH of about 3, and, after washing with water, the precipitate is collected and washed on a suitable filtering crucible. The precipitate is then dissolved in concentrated hydrochloric acid, and treated with a measured excess of standard potassium bromate solution. A measured excess of the arsenite solution is then added and the excess titrated with the standard bromate. Care must be taken to prevent the escape of bromine by the addition of arsenite after the reaction. A special technique is required to do this.

**Separation of copper and iron.** When salicylaldoxime is added to an acetic acid solution containing copper and ferric salts, the precipitate of copper salicylaldoximate is contaminated with a soluble ferric complex.<sup>14</sup> This effect, however, can be minimized by the addition of a little hydrochloric acid.<sup>5</sup> Reif<sup>15,24</sup> has developed a method for the microdetermination of copper in the presence of iron in which tartaric acid is used to eliminate interference by the latter metal.

**Reagent.** Dissolve 5 g. of salicylaldoxime in 100 ml. of alcohol.

**Procedure.** Determine approximately the iron content of the sample and add 20 times as much tartaric acid as there is iron present. Dilute the acid solution with water until all of the solid has dissolved, and then add ammonium hydroxide until the solution turns green. Acidify by the dropwise addition of a cold saturated solution of ammonium acetate, and then add a slight excess of the salicylaldoxime reagent. Allow the mixture to stand for 20-30 minutes, and then filter through a filtering crucible. Wash, dry at 105° C. and weigh as the oximate. The factor for copper is 0.1895.

Excellent results are reported with this method. Shik,<sup>17</sup> however, finds that this method is accurate only for small quantities of iron, and that it does not give reliable results in the presence of zinc, nickel and cobalt in acetic acid.

Ubal dini<sup>12</sup> has used salicylaldoxime for the determination of copper in pyrites, and Jean<sup>38</sup> for the determination of copper in steel.

**Separation of copper from cadmium.** Cadmium is not precipitated with salicylaldoxime unless the solution is neutral or basic, while the copper salt is precipitated from an acid solution; consequently, copper can be quantitatively separated from cadmium with salicylaldoxime by a proper control of pH.<sup>25,29</sup> If copper is to be determined by weighing the precipitate as  $\text{Cu}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ , the pH value of the acetic acid solution must be 2.6 or greater,<sup>14</sup> but if the reagent is used only to separate copper from the solution, the excess of acetic acid is not critical. After separating cadmium from the copper complex by filtration, cadmium may be determined in the filtrate electrolytically. The presence of an excess of the reagent in the filtrate is favorable to the deposition of cadmium. Stengel<sup>29</sup> has reported a method for determining copper in iron and steel, particularly in the presence of alloying elements.

Salicylaldoxime may also be used for the separation of copper and cadmium in qualitative analysis.<sup>28</sup>

**Reagent.** Dissolve 10 g. of salicylaldoxime in 50 ml. of ethyl alcohol, and pour this solution into 950 ml. of water that has been heated to 80° C. Stir, cool and filter.

**Procedure.** Add acetic acid to the blue ammoniacal solution of copper (and possibly cadmium) which is obtained in the usual scheme of qualitative analysis until the mixture is acid to litmus. Then add the reagent solution until precipitation is complete. The copper salt is yellow-green. Filter, test the filtrate for complete precipitation, and then test for cadmium with hydrogen sulfide.

**Separation of copper and lead.** Recent work by Biefeld and Howe<sup>14</sup> and Ligett and Biefeld<sup>30</sup> shows that copper may be easily separated from lead with salicylaldoxime by a proper control of the acidity of the solution. The pH is usually adjusted by means of acetic acid. If copper alone is to be determined, the simplest procedure is to buffer the solution with an acetate to insure the complete precipitation of copper. This is not satisfactory, however, if lead is to be determined in the filtrate after precipitating copper with salicylaldoxime, since the lead complex is appreciably soluble in acetate solutions.<sup>9</sup> The correct pH for the precipitation may readily be obtained by the use of a modified methyl orange indicator. After the addition of the reagent to a solution containing copper and lead, add 1 or 2 drops of the indicator, and neutralize with ammonia, and finally neutralize by the dropwise addition of 0.5 M ammonium hydroxide with stirring. Upon standing for a few minutes the supernatant liquid shows the acid color of the indicator. It is not necessary to neutralize the solution again.<sup>31</sup>

Salicylaldoxime may be used for the determination of copper in bearing metals.<sup>16</sup>

**Separation of nickel and copper.** Biefeld and Howe<sup>14</sup> have determined the effect of pH upon the precipitation of copper and nickel with salicylaldoxime, and have found that this reagent may be used satisfactorily for the separation of these metals. Salicylaldoxime precipitates copper quantitatively at a pH as low as 2.6, but the nickel precipitate does not begin to form until pH 3.3, and precipitation is not complete below pH 7.0. If the pH of the solution is kept between 2.6 and 3.1, all copper is precipitated with very little entrainment. A method for the determination of copper in copper-nickel alloys is reported by Chambers,<sup>32</sup> who states that cobalt and titanium interfere.

The following procedure for separating copper and nickel has been used by Riley:<sup>8</sup>

**Procedure.** To the solution of copper and nickel sulfates, add 1 g. of sodium acetate and 10 ml. of glacial acetic acid, and then dilute to 100 ml. Add an excess of 1 per cent salicylaldoxime solution and stir well. Allow to stand overnight and filter through a Gooch filter. Wash with cold water, dry at 100° C. and weigh.

Add dilute ammonium hydroxide to the filtrate until the mixture just remains acidic. Stir the nickel precipitate and filter. Wash until the filtrate gives no test with ferric chloride. The factor for nickel is 0.17742.



This method is said to give good results even with a copper-nickel ratio of 5:1.

**Detection and determination of iron.** Ferric iron forms a brown-violet, soluble complex with salicylaldoxime. This was first observed by Ephraim<sup>5</sup> who made this reaction the basis for a method of determining the point when precipitated copper and nickel complexes are washed free of contaminants in the procedure for the gravimetric determination of copper and nickel. In this procedure solutions of ferric chloride are added to successive portions of the washings of the precipitates until no color appears, thereby indicating the absence of salicylaldoxime.

Howe and Mellon<sup>38</sup> have studied the ferric salicylaldoxime complex to determine its applicability to the colorimetric determination of small quantities of ferric iron, and report that results are satisfactory. The color developed by salicylaldoxime in the presence of ferric iron is purple at pH 3 and yellow at pH 10. Between these two values, the colors of the solution appear as various combinations of these hues. The color of the product formed in a neutral solution is red-orange. A careful control of the acidity is imperative in order to obtain a reproducible hue and intensity of color. A pH of 7 appears to be the most satisfactory value, because of the ease with which this acidity may be maintained, and the lack of variation of transmittancy at the neutral point. An ammonium acetate solution, having a pH of almost 7, is used as the buffer. The solution obeys Beer's law over a rather wide concentration range, and may be used in a variable-depth type comparator. The following procedure may be used for the determination of iron:

**Reagent.** Prepare a 0.1 per cent solution of the reagent by dissolving the weighed solid in 5 ml. of ethyl alcohol and diluting to the proper volume with redistilled water. The solution should be prepared the day it is used.

**Procedure.** Weigh a quantity of sample containing 0.01-1.0 mg. of iron, and transfer to a 250-ml. Erlenmeyer flask. Dissolve, if solid, by digesting with 10 ml. of 1:3 nitric acid, and boil to expel the oxides of nitrogen. Cool, and add 10 ml. of 3 per cent hydrogen peroxide to oxidize the iron to the ferric state. Interference by nickel and copper may be eliminated as follows: Add sodium carbonate to the acid solution until dark red colloidal iron is formed. Then add salicylaldoxime in excess and filter the precipitate from the solution.

Cobalt, molybdenum, uranium, and chromium should be absent, or removed from the solution at this point. Phosphate may be precipitated by treating with a zirconyl salt, and the excess zirconium is eliminated by a subsequent procedure. Fluoride and borate may be destroyed by boiling with perchloric acid.

Make the solution just basic to litmus, and then add hydrochloric acid cautiously until the solution is just acid to litmus. Filter any insoluble material and wash the precipitate thoroughly. Combine the filtrate and the washings, and add 10 ml. of a 0.1 per cent solution of salicylaldoxime and stir well. Then add about 1 g. of ammonium acetate, dilute to 100 ml. in a volumetric flask, and mix well.

The unknown is compared in Nessler tubes with a series of standards similarly prepared. The comparison may be made in a colorimeter.

Many ions interfere with the above determination, but these may easily be removed. Tartrate, citrate, oxalate, cyanide, carbonate, borate and phosphate interfere seriously, probably because of the formation of complex ions. Fluoride, which also forms a complex with iron, may be present in quantities up to 10 mg. with 0.2 mg. of iron without serious consequence. Reducing ions such as iodide and sulfite also lead to erroneous results, but these ions may be removed by a preliminary oxidation. Zinc, mercury, lead, aluminum and beryllium interfere if an insufficient quantity of the reagent is used, but with an excess of salicylaldoxime, the presence of these ions is not objectionable. Molybdate, cobalt and uranyl ions form soluble colored complexes with salicylaldoxime and should be removed. Ions which hydrolyze to form hydrated oxides in neutral solutions also interfere, but these may be removed by filtration. Since the soluble ferric complex is entrained when copper is precipitated with salicylaldoxime in the presence of a ferric salt, copper and other metals which are precipitated as complexes may interfere with the colorimetric determination of iron. Copper may be separated from iron with salicylaldoxime before the latter metal is determined by using a gravimetric precipitation with ammonium hydroxide. When the iron solution is filtered from the precipitated copper salicylaldoximate, ferric hydroxide cannot be precipitated from the filtrate with ammonium hydroxide until the reagent has previously been oxidized with bromine.

**Determination of zinc.** The formation of an insoluble complex of zinc with salicylaldoxime was first reported by Ephraim.<sup>5</sup> Pearson<sup>34</sup> studied the properties of zinc salicylaldoximate and concluded that it is not suitable for the determination of zinc because the pH range for complete precipitation is too limited. The precipitate is appreciably soluble in various neutral salt solutions, and the compound slowly decomposes above 80° C. From solutions of pH 7-8, the precipitate obtained with salicylaldoxime corresponds to the formula  $\text{Zn}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ , but attempts to determine zinc by precipitation in this form give extremely variable results, depending upon factors such as the time of standing before filtration. Flagg and Furman<sup>9</sup> found that if zinc salicylaldoximate, together with the solution from which it has been freshly precipitated, is warmed to 90° C. for 10 minutes, the monosalicylaldoximate  $\text{ZnC}_7\text{H}_5\text{O}_2\text{N}$  is formed. This compound contains 32.61 per cent of zinc and can be dried at 110° C. without decomposition. The precipitation of zinc with salicylaldoxime is complete only in the pH range 7.1 to 8.1. The compound is completely soluble below pH 5.8 and above pH 9.7 if the pH is regulated with ammonia.<sup>31</sup>

**Determination of cadmium.** Cadmium is precipitated by salicylaldoxime under the same conditions as zinc, but the precipitate appears to be a variable mixture of the mono- and disalicylaldoximates.

**Determination of nickel.** A method for determining nickel with salicylaldoxime has been investigated by Riley.<sup>8</sup> Copper and other metals which yield precipitates in acid solutions are removed by precipitating with salicylaldoxime in an acetic acid solution, and nickel is then precipitated by neutralizing the filtrate with ammonium hydroxide. The nickel precipitate has the composition  $\text{Ni}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ . The factor for nickel is 0.17742. Iron, mercury,

silver and zinc do not interfere, although cobalt yields a precipitate in neutral solutions.

**Determination of lead.** Ishabishi and Kishi<sup>27,85</sup> suggested the use of salicylaldoxime for the determination of lead. The lead salt is precipitated from a strongly ammoniacal solution and weighed after drying at 105° C. The lead salt corresponds to the formula  $\text{PbC}_7\text{H}_5\text{O}_2\text{N}$ . According to a more recent study by Ligett and Biefeld,<sup>80</sup> lead can be determined by precipitation as the salicylaldoximate as proposed by Ishabishi and Kishi,<sup>85</sup> but several refinements in the procedure are indicated. From nitrate solutions, precipitation of the lead salt begins at a pH just above 4.8 and is complete at a pH of 6.9. The precipitate obtained at pH 6.9, however, does not have a composition represented by the formula  $\text{PbC}_7\text{H}_5\text{O}_2\text{N}$ . Precipitation must be carried out at a pH of 8.9 or above in order to obtain the compound corresponding to the above formula, and to which the theoretical factor 0.6053 for lead can be applied. When acetate ions are present in concentrations as low as 0.05 M, it is necessary to increase the pH for beginning the precipitation, for complete precipitation, and for complete precipitation as lead salicylaldoximate. This increase is approximately 0.5 pH unit.

The following procedure may be employed for the determination of lead:

**Reagent.** Dissolve 1 g. of salicylaldoxime in 5 ml. of 95 per cent ethyl alcohol and pour slowly into 95 ml. of water that has been heated to 80° C. Cool and filter before using. This reagent should be used the same day that it is prepared.

**Procedure.** Add 10 ml. of the reagent to about 25 ml. of a solution containing 0.5-0.1 g. of lead as the nitrate or acetate, and then add ammonium hydroxide until the pH is approximately 9.5. Then dilute to 65 ml. and stir. Allow to stand for 1 hour, wash by decantation, and filter with suction through a No. 4 Jena filter crucible. Wash with water until the precipitate is free of the reagent as shown by the absence of coloration of the filtrate upon the addition of a little ferric chloride solution. Dry at 105° C. for 1 hour and weigh as  $\text{PbC}_7\text{H}_5\text{O}_2\text{N}$ . The factor for lead is 0.6053.

Since a number of metal salicylaldoximates are readily soluble in ammonium hydroxide, some separations of lead from other metals are possible by the above method. The quantity of ammonia required to dissolve the salicylaldoximates of a few of the common metals is shown in Table 46.

To obtain these data, solutions were prepared exactly as described in the above procedure except that no ammonium hydroxide was added. Then after adding 1 drop of 4 M ammonia to cause precipitation of the metal salicylaldoximate, concentrated ammonium hydroxide was added dropwise with stirring to determine the solubility of the metal complex. The bismuth, ferrous, magnesium, manganese and mercuric salicylaldoximates do not dissolve in ammonia solutions in concentrations up to 8 M. Lead can be separated from silver, cadmium and zinc by precipitating with salicylaldoxime from strongly ammoniacal

solutions, but by using the same procedure lead cannot be separated from one or more of the following metals: nickel, cobalt, copper, mercury, manganese, bismuth, iron and magnesium.

TABLE 46.—AMMONIA REQUIRED TO DISSOLVE METAL SALICYLALDOXIMATES

-Metal Salicylaldoximate	Volume Concentrated Ammonia Added ml.	Concentration of Ammonia in Resulting Solution molar
Silver	0.05	0.01
Zinc	0.4	0.1
Cadmium	1.2	0.3
Nickel	6.6	1.5
Cobalt	6.7	1.5
Copper	50.0	7.0

A fairly wide range of ammonia concentrations is sufficient to prevent the precipitation of zinc as the salicylaldoximate while still permitting the complete precipitation of lead, provided a large quantity of ammonium nitrate is present. In the absence of ammonium nitrate, however, the permissible range of ammonia concentration is much less.

Copper may be precipitated by adding salicylaldoxime to a slightly acid solution containing copper and lead ions, while the lead remains in solution and is separated from copper by filtration; lead is then precipitated from the filtrate by adding ammonium hydroxide until the pH is 8.9. It may be necessary to add more reagent to effect complete precipitation of lead.

Biefeld and Ligett<sup>31</sup> have studied the precipitation of zinc with salicylaldoxime, and report that the reagent may be used for a satisfactory separation of lead from zinc, and for the separation of metals containing copper, lead and zinc. A procedure which may be used for the determination of copper, lead and zinc in solutions containing varying proportions of these metals is carried out as follows:

**Procedure.** Add 30 ml. of a 1 per cent solution of salicylaldoxime to the solution containing copper, lead and zinc, and make neutral to a modified methyl orange indicator by the dropwise addition of 0.5 M ammonium hydroxide. Allow the mixture to stand for 30 minutes and filter on a Gooch crucible. Wash with 20 per cent alcohol and dry at 110° C. and finally weigh as  $\text{Cu}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ . The factor for copper is 0.1893.

Transfer the filtrate to a beaker and add 0.7 g. of ammonium nitrate and 1.0 ml. of concentrated ammonium hydroxide for each 10 ml. of the solution. Under these conditions, lead is precipitated as the salicylaldoximate. Allow the mixture to stand for 1 hour, filter the precipitate on a Gooch crucible. Wash with 20 per cent alcohol, dry at 110° C. and weigh as  $\text{Pb}(\text{C}_7\text{H}_5\text{O}_2\text{N})$ . The factor for lead is 0.6053. Zinc may be determined in the filtrate by precipitating and weighing as  $\text{ZnNH}_4\text{PO}_4$ .

The quantities of metals for which this procedure has been successful range from 9-45 mg. of copper, 40-60 mg. of lead and 45-70 mg. of zinc.

The separation of lead from zinc in a strongly ammoniacal solution is improved by the addition of a large quantity of ammonium nitrate. Zinc cannot be quantitatively precipitated as the salicylaldoximate in the strongly ammoniacal filtrate obtained from the lead separation.

**Determination of palladium.** When a slightly acidified solution containing tetravalent palladium is treated with a hot, saturated, and filtered solution of salicylaldoxime in water, a yellow precipitate is obtained which can be washed with water and cold 30 per cent alcohol and then dried at 110° C. and weighed. The precipitate contains 28.17 per cent palladium.<sup>6</sup>

Gahide<sup>7</sup> has suggested a different method for the determination of palladium: the metal is precipitated with a standard salicylaldoxime solution from an acid solution; and, after the precipitate is filtered and washed, the excess oxime is found by titration. 5-40 mg. of palladium can be determined by this method in the presence of other metals.

**Determination of bismuth.** Bismuth is quantitatively precipitated as the salicylaldoximate from solutions of pH 7.2 to 9.4 or higher.<sup>9,10</sup> The bismuth precipitate contains 57.3 per cent bismuth, which corresponds to no exact formula, although it approximates closely to the hypothetical substance  $(C_7H_5O_2N)BiOH$ . Since the precipitate is not definite in composition, and since it cannot be obtained in a weighable form, the most suitable method for determining bismuth is to ignite to  $Bi_2O_3$  before weighing:

**Procedure.** To the unknown solution, which should contain not more than 0.1 g. of bismuth for each 100 ml. of solution, add 1 g. of ammonium nitrate and 15 ml. of a 1 per cent salicylaldoxime solution for each 0.1 g. of bismuth contained in the sample. Heat to 50° C. and stir thoroughly, and then add 6 N ammonium hydroxide until the pH of the solution is at least 7.2. If bismuth is to be separated from silver, the pH should be 9. If bismuth is to be separated from zinc, the alkalinity should correspond to a pH of 10. Stir for 10 minutes, and allow the precipitate to settle. Filter through a weighed porcelain filter crucible and wash thoroughly with 1 M ammonium hydroxide. Dry for 30 minutes at 110° C., and add 0.3 g. of pure ammonium nitrate. Place the crucible within a larger porcelain crucible, and heat gently until the organic matter is destroyed, and then ignite at the full temperature of a Fisher burner. Ignite to constant weight and weigh as  $Bi_2O_3$ .

Bismuth can be separated from silver and zinc by the above procedure.

**Detection of vanadium.** Flagg and Furman<sup>9,10</sup> first observed the formation of a black precipitate when salicylaldoxime is added to a solution containing vanadic acid. The vanadic acid is only partially precipitated by salicylaldoxime from solutions containing sulfuric acid and the black compound appears to have a composition represented by the formula  $C_{21}H_{21}N_3O_{10}V_2$ . Only 25-50 per cent of the vanadium is precipitated from a solution that is 0.02 N in sulfuric acid, and 60-75 per cent from solutions which are 0.05-1.0 N in sulfuric acid. From 2 N sulfuric acid solutions, only 35 per cent of vanadium is pre-

precipitated. As little as 0.02 mg. of vanadium as vanadic acid in 15 ml. of solution may be detected by first adding salicylaldehyde and then 1 ml. of chloroform and shaking. The vanadium complex passes into the chloroform layer to which it imparts an orange to reddish-orange color. Ferric iron gives a similar reaction, although molybdenum and chromium do not interfere with this test.

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25. M. Ishibishi and H. Kishi, *J. Chem. Soc. Japan.* **55**, 1060-64 (1934); *C.A.* **29**, 702 (1935).
26. M. Ishibishi and H. Kishi, *J. Chem. Soc. Japan.* **55**, 1065 (1934); *C.A.* **29**, 702 (1935).
27. M. Ishibishi and H. Kishi, *J. Chem. Soc. Japan.* **55**, 1067-69 (1934); *C.A.* **29**, 702 (1935).
28. L. P. Biefeld, *J. Chem. Ed.* **18**, 525-6 (1941); *C.A.* **36**, 2226 (1942).
29. E. Stengel, *Tech. Mitt. Krupp, Forsch. Ber.* **2**, 87 (1939); *C.A.* **33**, 8521 (1939).
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31. L. P. Biefeld and W. B. Ligett, *Ind. Eng. Chem., Anal. Ed.* **14**, 359-61 (1942); *C.A.* **36**, 3747 (1942).
32. M. Chambers, *Chemist-Analyst.* **26**, 52 (1937); *C.A.* **31**, 6578 (1937).
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35. M. Ishibishi and H. Kishi, *Bull. Chem. Soc. Japan.* **10**, 362-8 (1935); *C.A.* **29**, 7858 (1935).
36. L. A. Mennucci, *Rev. facultad cienc. quim. (Univ. Natl. La Plata)* **17**, 165-76 (1942).
37. F. Pavelka and G. Setta, *Mikrochem. ver. Mikrochim. Acta* **31**, 73-82 (1943); *C.A.* **38**, 1974 (1944).
38. M. Jean, *Bull. soc. chim.* **10**, 201-4 (1943); *C.A.* **38**, 6230 (1944).

## CHAPTER IX

### MONOXIMES OF DIKETONES

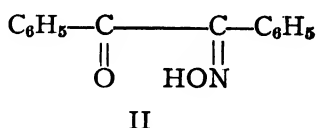
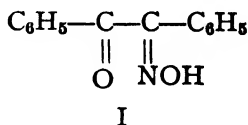
The group  $\text{—CO—C(=NOH)—}$ , which is contained in the monoximes of the diketones, is analytically important, since it confers upon the molecule the property of inner-complex formation. One of the most interesting reactions of compounds of this type is the so-called "iron-blue reaction," which was first observed by Whiteley.<sup>1</sup> Ferrous salts in solutions buffered with an acetate form inner-complex salts with numerous isonitroso compounds, which contain the oxime group through enolization. These complexes are usually deep blue in color, and are more or less soluble in water. They dissolve in organic solvents to form blue solutions.

The reactions of ferrous salts with isonitroso compounds is usually extremely sensitive. After the addition of ammonium hydroxide or disodium phosphate, Kröhnke<sup>2</sup> was able to obtain a positive test by shaking a chloroform solution of isonitrosoacetophenone,  $\text{C}_6\text{H}_5\text{—CO—CH=NOH}$ , with a solution of a ferrous salt containing as little as 0.03 mg. of iron per liter (page 279). Kuster<sup>3</sup> has found that a 0.0075 per cent solution of ferrous sulfate gives a distinct reaction with isonitrosoacetylacetone,  $\text{CH}_3\text{—CO—C(=NOH)—CO—CH}_3$ . Dubsky and Kuras<sup>4</sup> have used diisonitrosoacetone,  $\text{CH(CH=NOH)—CO—CH=NOH}$ , in a very sensitive test for iron. While sensitive, these reactions are rarely used in analytical practice, since more convenient procedures employing dimethylglyoxime and 2,2'-dipyridyl are available.

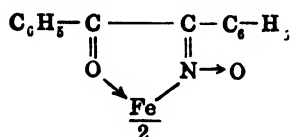
In order to establish the relationship between structure and the iron-blue reaction with ferrous iron, Feigl and co-workers<sup>5,6</sup> investigated the reactions of a number of monoximes of diketo compounds. They found that isonitrosoacetone, isonitrosomethyl ether, diisonitrosoacetone, isonitrosoacetylacetone, isonitrosomethylethyl ketone, isonitrosoacetoacetic ester, bromoisonitrosoacetoacetic ester; isonitrosoacetophenone, isonitrosobenzoylacetone and isonitrosocyanacetamide all give blue colors with ferrous salts. Dibromoacetoacetic ester gives a red color, isonitrosocinnamalacetone a green color and isonitrosocyanacetylurea a violet color. On the other hand, tribromoisonitrosoacetoacetic ester, chloroisonitrosoacetophenone and isonitrosobenzoylacetacetic ester, which are not enolizable, do not give a reaction with ferrous salts. From these studies it appears evident that the iron-blue reaction is obtained only with those compounds in which there is an enolizable carbonyl group in proximity to the oxime group. For example, isonitrosoacetophenone,  $\text{C}_6\text{H}_5\text{—CO—CH=NOH}$ , gives the iron-blue reaction, while the chloro derivative,  $\text{C}_6\text{H}_5\text{—CO—CCl=NOH}$ , in which there is no possibility of enolization, does not react with ferrous iron. This conclusion is further emphasized by a study of isonitrosoacetoacetic ester and its bromosubstitution products: isonitrosoacetoacetic ester,  $\text{CH}_3\text{—CO—C(=NOH)—CO}_2\text{R}$ , and the mono, and dibromo substitution products,  $\text{CH}_2\text{Br—CO—C(=NOH)—CO}_2\text{R}$  and  $\text{CHBr}_2\text{—CO—C(=NOH)—CO}_2\text{R}$ , are enolizable, and give the iron-

blue reaction, while the tribromo derivative,  $\text{CBr}_3\text{—CO—C(=NOH)—CO}_2\text{R}$ , which is not enolizable, is not reactive.

Factors other than enolizability, however, are important in determining the iron-blue reaction. For example,  $\alpha$ -benzilmonoxime (I) reacts with ferrous iron to give a blue color, while  $\beta$ -benzilmonoxime (II) is unreactive.

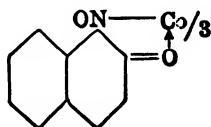


There is no possibility of enolization in either compound, but the steric arrangement of the oxime group in  $\alpha$ -benzilmonoxime is such that the complex salt



is formed. The configuration of the  $\beta$ -isomer is such that a similar complex is impossible.

A number of analytically important compounds containing the grouping  $\text{—CO—C(=NOH)—}$  are known in which the two carbon atoms are a part of a ring structure. Best known of these are  $\alpha$ -nitroso- $\beta$ -naphthol,  $\beta$ -nitroso- $\alpha$ -naphthol and  $o$ -nitrosophenol. These compounds form intensely colored, slightly soluble complexes with almost all of the heavy metals. The cobaltic salt of  $\alpha$ -nitroso- $\beta$ -naphthol, for example, is derived from the tautomeric quinoneoxime form of the compound.

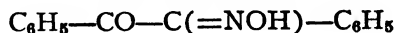


### $\alpha$ -BENZILMONOXIME

$\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}$

Mol. Wt. 225.23

Beil. Ref. VII, 757.



**Use:** Reaction with cobalt.

$\alpha$ -Benzilmonoxime is obtained as leaves from benzene or methyl alcohol. It melts at  $137\text{--}8^\circ\text{C}$ . It is easily soluble in cold alcohol, ether, acetic acid, and chloroform, and is somewhat less soluble in carbon disulfide and benzene.

**Preparation:** Grind pure benzil to a thin paste with a little alcohol, and add 1 equivalent of hydroxylamine hydrochloride in a concentrated aqueous solution. Cool the mixture to  $-5^\circ\text{C}$ . with the aid of a bath of crushed ice and concentrated hydrochloric acid. Then add dropwise 3 equivalents of sodium hydroxide



in a 20 per cent aqueous solution with rapid mechanical stirring. The temperature must not rise above 0° C., and the stirring must be efficient. After 1.5 hours, dilute with water and filter any unchanged benzil through a sintered glass filter. Acidify the filtrate with a minimum of glacial acetic acid, and allow to stand until the oxime separates. Filter and recrystallize from 60 volume per cent aqueous alcohol. Then recrystallize twice from benzene.<sup>1,2</sup>

**Reaction with cobalt.** When  $\alpha$ -benzilmonoxime is added to a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  containing sodium acetate, a red compound is formed which corresponds in composition to that of the ferrous salt (above).

This compound is insoluble in water, slightly soluble in alcohol or acetic acid, soluble in benzene, chloroform, and acetone. It is very resistant toward the action of hot acids and alkalis. It may be formed according to the following procedure:<sup>3</sup>

**Procedure.** Dissolve 0.6 g. of  $\alpha$ -benzilmonoxime in 10 ml. of alcohol, heat to boiling, and mix with 3 ml. of an alcoholic solution of cobalt chloride or nitrate containing 0.02 g. of cobalt per ml., and with 1.5 ml. of an alcoholic solution of ammonium acetate containing 0.3 g. of ammonium acetate. Heat and allow to cool.

1. M. O. Forster and P. C. Dunn, *J. Chem. Soc.* **95**, 431 (1909).
2. T. W. J. Taylor and M. S. Marks, *J. Chem. Soc.* **1930**, 2305.
3. P. Pfeiffer and J. Richarz, *Ber.* **61B**, 103-7 (1927); *C.A.* **22**, 1291 (1928).

## DIACETYLMOXIME

$\text{C}_4\text{H}_7\text{O}_2\text{N}$

Mol. Wt. 101.10

Beil. Ref. I, 772.



**Use:** Detection and determination of nickel.

Diacetylmonoxime is a crystalline solid melting at 74° C. and boiling at 185-86° C. It is only slightly soluble in water, but dissolves readily in alcohol, ether and chloroform.

**Preparation:** Mix 85 g. of methyl ethyl ketone with 3 ml. of concentrated hydrochloric acid, and then add dropwise 100 ml. of amyl nitrite over a period of 2 hours with stirring and cooling. The temperature should not exceed 50° C. during the addition of the nitrite. Next add 80 g. of ice and 80 g. of 33 per cent sodium hydroxide to the mixture, and extract the amyl alcohol which is formed with a large quantity of ether. Acidify the alkaline solution with dilute sulfuric acid while keeping the temperature below 10° C. by the addition of ice. Wash the crystalline residue which forms with a little water and melt over a water-bath. After the mass has solidified remove the oxime as a crystalline lump from the mother liquor. Purify by recrystallizing from water.<sup>1</sup>

**Detection and determination of nickel.** Mironoff<sup>2</sup> has suggested the use of diacetylmonoxime for the detection and determination of nickel, with

which it reacts in a manner similar to that of dimethylglyoxime. Wenger and co-workers<sup>3</sup> have recommended the use of a 4 per cent alcoholic solution of diacetylmonoxime as a spot test for nickel. The solution to be tested is made alkaline with ammonium hydroxide, and then treated with a few drops of the reagent. A red precipitate indicates the presence of nickel. The test is said to be sensitive to 1  $\gamma$  of nickel in 1 ml. of solution. Cobalt interferes by forming a brown color.

Mironoff<sup>2</sup> used diacetylmonoxime in a titration procedure for the determination of nickel. The nickel is precipitated as the oxime, the washed precipitate is then boiled with an excess of ferric iron, and the resulting ferrous iron determined with potassium permanganate. For the details of this procedure, see section on dimethylglyoxime, page 197.

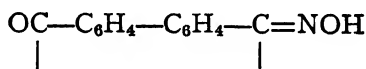
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3. P. Wenger, R. Duckert and M. Busset, *Helv. Chim. Acta.* **24**, 889-99 (1941); *C.A.* **36**, 2225 (1942).

### PHENANTHRENEQUINONEMONOXIME

$C_{14}H_9O_2N$

Mol. Wt. 223.21

Beil. Ref. VII, 803(418).



**Use:** Detection of metals.

This compound is obtained as greenish-yellow needles from alcohol, and crystallizes from benzene as orange-colored leaves. It melts at 158° C., and is readily soluble in hot alcohol.

**Preparation:** Suspend 1 mole of phenanthrenequinone and 1 mole of hydroxylamine in a mixture of 15 parts of alcohol and 2.5 parts of chloroform, and heat under reflux for one hour on a boiling water bath. Cool, collect the crystals which form, and recrystallize from boiling alcohol.<sup>1,2</sup>

**Reactions with metals.** Pavolini<sup>3</sup> has used an alcoholic solution of phenanthrenequinonemonoxime as a reagent for the detection of ferrous, cuprous, cobalt and nickel ions. The color reactions of these ions are shown in Table 47.

TABLE 47.

Ion	Color
Ferrous Cuprous Cobalt Nickel	Blue-green Cochineal Yellow-ochre Maroon

More recently Keuning and Dubsky<sup>4,5</sup> have studied the reactions of various metallic ions with this reagent. Their results are reported in Table 48.

TABLE 48.

As reagent, use a 0.02 N solution of phenanthrenequinonemonoxime in 50 ml. of ethyl alcohol, and mix this with a 0.1 N solution of the ion.

Ion or Compound	Result
Lead acetate	Orange precipitate
Mercurous	Red precipitate, which dissolves on heating
Mercuric	Red precipitate, which remains insoluble on heating
Silver	Yellow precipitate ( $C_{14}H_8O_2NAg$ ), upon which another mole of $C_{14}H_8O_2N$ is added or adsorbed
Copper	Reddish-brown precipitate
Nickel	Chocolate-colored precipitate
Cobalt	Red precipitate
Ferric	Reddish-brown precipitate
Ferrous	Green precipitate
Chromium	Green precipitate
Thallous hydroxide	Green needles

Most of the salts formed by reactions of phenanthrenequinonemonoxime with cations are internal complexes which readily adsorb or add definite quantities of the free oxime. In 80 per cent acetic acid, the lead, mercury, ferrous and chromium precipitates dissolve quickly, the silver, nickel and ferric precipitates dissolve only slowly while the copper and cobalt precipitates remain insoluble. The lead mercurous, copper, nickel, cobalt and ferric precipitates do not dissolve in concentrated ammonia, although some of them change color.

1. H. Goldschmidt, *Ber.* **16**, 2178 (1883).
2. H. Goldschmidt, *Ber.* **22**, 1989 (1889).
3. T. Pavolini, *Industria Chimica*, **5**, 862 (1930); *C.A.* **24**, 5669 (1930).
4. K. J. Keuning and J. V. Dubsky, *Chem. Obzor.* **15**, 18-20 (1940); *C.A.* **34**, 6185 (1940).
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## CHAPTER X

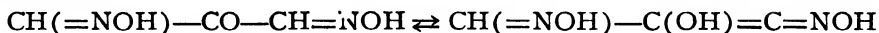
### ISONITROSO COMPOUNDS

#### DIISONITROSOACETONE

$C_3H_4O_3N_2$

Mol. Wt. 116.06

Biel. Ref. I-806(413).



**Use:** Detection of cobalt, copper, iron and nickel.

Diisonitrosoacetone is obtained as glistening crystals from methyl alcohol. These decompose at 143-144° C. The compound is only slightly soluble in water, chloroform and benzene, but is easily soluble in alcohol and ether.

**Preparation.** *Acetonedicarbonic acid:* Mix 2 parts of finely powdered hydrated citric acid with 1 part of fuming sulfuric acid (18.3 per cent), and heat on a water bath at 65-70° C. without agitation. Heat for about 1 hour and allow the reaction to continue for about 5 minutes after the flame of carbon monoxide is extinguished. Cool the mixture to 0° C. and add 500 ml. of water in small portions, cooling thoroughly after each addition. After 200 ml. of water has been added, crystals begin to form. Then add the remainder of the water and filter through an 8-inch Büchner funnel, and press the mass down with a pestle or similar instrument until no longer sticky.<sup>1,2,3</sup>

*Diisonitrosoacetone:* Place 50 g. of the crude acetonedicarbonic acid in a 500 ml. flask and add 100 ml. of water. Cool the mixture with ice water, and slowly add with occasional shaking a cold saturated solution containing 40 g. of sodium nitrite. The reaction which follows is accompanied by considerable foaming, and a crystalline powder separates, and the odor of hydrogen cyanide may be detected. After all the sodium nitrite solution is added, add dilute hydrochloric acid in small quantities until a precipitate is no longer formed. Then place the flask and contents in a cooling mixture, and filter quickly with suction. Treat the residue with cold water.<sup>1,2,3</sup>

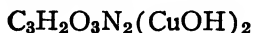
**Detection of iron.** Ferrous iron may be detected by means of intense blue coloration which appears when a solution of ferrous salt is treated with diisonitrosoacetone and then neutralized with ammonium acetate.<sup>4</sup> If the solution is dilute, the color appears only on standing. The test may be made as follows:

**Procedure.** Add 5 ml. of solution of ferrous salt to 1 ml. of 1 per cent solution of diisonitrosoacetone and then neutralize with ammonium acetate. The reaction is said to be 100 times more sensitive than that with dimethylglyoxime.

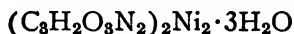
The reaction is sensitive in dilutions of 1:10,000,000. Ferric iron does not give this reaction, but may be easily reduced to the ferrous state by means of

hydrazine or hydrazine sulfate. Cobalt and nickel prevent the formation of the blue color, and an excess of manganese decreases the sensitivity of the reaction.

**Reaction with copper, ferric iron, cobalt and nickel.** Diisonitrosoacetone reacts with solutions of copper acetate to give a dark green compound corresponding in composition to the formula,<sup>5</sup>



Diisonitrosoacetone also reacts with an ammoniacal solution of nickel chloride to yield a yellow compound having the following composition,



When diisonitrosoacetone is added to a solution of ferric chloride, and the mixture made alkaline with ammonia, dark green needles are formed. With cobalt chloride and sodium acetate a red compound is formed.

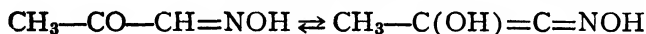
1. K. K. Koessler and M. T. Hanke, *J. Am. Chem. Soc.* **40**, 1718 (1918).
2. H. v. Pechmann, *Ann.* **261**, 155 (1891).
3. H. v. Pechmann and K. Wehsarg, *Ber.* **19**, 2465 (1886).
4. J. V. Dubsky and M. Kuras, *Chem. Listy.* **23**, 496 (1929); *C.A.* **24**, 801 (1930).
5. J. V. Dubsky, Fr. Brychta, and M. Kuras, *Pub. faculte sci. univ. Masaryk.* **129**, 1-26 (1931); *C.A.* **26**, 2943 (1932).

## ISONITROSOACETONE

$\text{C}_3\text{H}_5\text{O}_2\text{N}$

Mol. Wt. 87.08

Biel. Ref. I-763(396).



**Use:** Detection of cadmium, cobalt, copper, iron, lead, manganese, mercury, tin and zinc.

Isonitrosoacetone is obtained as crystalline leaves from ether. It melts at 69° C., sublimes easily, and is volatile with steam. It is easily soluble in water and ether, and is only moderately soluble in chloroform, carbon tetrachloride and benzene.

**Preparation:** Dissolve 4.5 g. of acetoacetic ester in a solution prepared by dissolving 2.1 g. of potassium hydroxide in 80 ml. of water, and allow to stand 24 hours. Then add to this mixture 2.5 g. of sodium nitrite dissolved in 10 ml. of water, and acidify the solution with sulfuric acid. Make alkaline, and then again acidify, keeping the mixture cool during these operations. The isonitrosoacetone separates from the liquid as a crystalline solid. Remove the oily material by pressing the crystals between sheets of filter paper.<sup>1,2,3</sup>

The following method is described by Küster:<sup>4</sup> Dissolve 5.8 g. of acetone in 30 ml. of glacial acetic acid, and cool the mixture to 0° C. To this slowly add dropwise a concentrated aqueous solution of 15 g. of sodium nitrite. Allow to stand 45 minutes and add 100 ml. of water, and then extract the mixture with ether. Wash the ether solution several times with 10 ml. portions of water and dry with sodium sulfate. Remove the ether by distillation. Dry the residual crystals on a porous plate, and then recrystallize from benzene.

**Reactions.** Isonitrosoacetone reacts with cupric acetate in the presence of sodium acetate to yield a green amorphous compound, which is a typical inner-complex.

With ferrous ammonium sulfate, and in the presence of sodium acetate, isonitrosoacetone reacts to form a blue salt (page 272). Similar compounds are formed when isonitrosoacetone is added to solutions of various metallic salts. These are summarized in Table 49.<sup>5</sup>

TABLE 49.

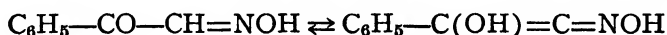
Salt	Medium	Reaction	Remarks
ZnCl <sub>2</sub>	NH <sub>3</sub>	Yellow needles	Changes to yellow-red with NH <sub>3</sub>
FeCl <sub>3</sub>	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Red-yellow color	
CoCl <sub>2</sub>	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Orange colored	
Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	NH <sub>3</sub>	Yellow color	
HgNO <sub>2</sub>	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Crystalline needles	
CdSO <sub>4</sub>	NH <sub>3</sub>	Yellow needles	
SnCl <sub>2</sub>	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	White needles	
MnCl <sub>2</sub>	NH <sub>3</sub>	Orange-yellow needles	

1. M. Ceresole, *Ber.* 15, 1326 (1882).
2. V. Meyer and J. Zublin, *Ber.* 11, 695 (1878).
3. L. Claisen, *Ber.* 20, 252 (1887).
4. W. Küster, *Z. physiol. Chem.*, 155, 174 (1926).
5. J. V. Dubskey, Fr. Brychta, and M. Kuras, *Pub. faculte sci. univ. Masaryk.* 129, 1-26 (1931); *C.A.* 26, 2943 (1932).

## ISONITROSOACETOPHENONE

Synonym: Benzoylformaldoxime, phenylglyoxaldoxime

C<sub>8</sub>H<sub>7</sub>O<sub>2</sub>N                      Mol. Wt. 149.14              Beil. Ref. VII, 671 (361).



**Use:** Detection of cobalt, iron, lead, manganese, mercury and nickel.

Isonitrosoacetophenone is a white crystalline solid melting at 126-128° C. It is only slightly soluble in cold water and somewhat more soluble in hot water. It is soluble in chloroform, in alkalis, and in alkali carbonates.

**Preparation:** Dissolve 1 mole of sodium in 20 times its weight of absolute alcohol, and to this solution add in small portions, and with cooling, first 1 mole of amyl nitrite and then 1 mole of acetophenone. Allow this mixture to stand 1-2 days in a well-stoppered bottle, and keep cool. At the end of this time, filter off the brown sodium salt, wash with ether, and dry in air. To convert the sodium salt to the free isonitroso ketone, dissolve in ice water and add the calculated quantity of glacial acetic acid. Filter the yellow precipitate with suction, dry and recrystallize from ethyl acetate or chloroform.<sup>1,2</sup>

**Detection of iron.** Claisen<sup>1</sup> first observed that isonitrosoacetophenone reacts with solutions of ferrous ions to give an intensely blue colored compound.

Krohnke<sup>3,4</sup> has used this reaction for the detection of as little as 3 parts of ferrous iron in 100,000,000 parts of water.

**Reagent.** Dissolve 1.49 g. of isonitrosoacetophenone in 100 ml. of chloroform.

**Procedure.** Mix 1 ml. of a solution of a ferrous salt with 1 ml. of the chloroform solution of isonitrosoacetophenone. Make the mixture slightly alkaline, preferably with disodium phosphate, and shake. The aqueous layer remains colorless, and the chloroform layer is colored blue.

Isonitrosoacetophenone forms inner-complex salts with many bivalent metals, such as nickel, cobalt, manganese, lead and mercury, which give characteristic colors. These metallic complexes are similar in composition to that of the ferrous salt (page 272).<sup>5</sup>

**Detection of nickel and cobalt.** Nickel and cobalt can be identified in the same solution by using a procedure suggested by Krohnke.<sup>3</sup>

**Procedure.** Mix 1 ml. of a solution containing nickel and cobalt ions with 1 ml. of a chloroform solution containing 1.49 g. of isonitrosoacetophenone, and make alkaline with disodium phosphate. If nickel is present the chloroform layer is red-brown in color. Now make acid with 25 per cent acetic acid, whereupon a reddish-yellow color appears in the chloroform layer if cobalt is present.

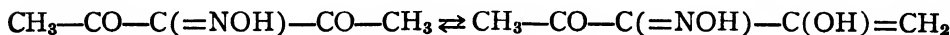
1. L. Claisen, *Ber.* 20, 656 (1887).
2. L. Claisen, O. Manasse, *Ber.* 20, 2194 (1887).
3. F. Krohnke, *Ber.* 60B, 527-30 (1927); *C.A.* 21, 1605 (1927).
4. F. Krohnke, *Gas-Wasserjach.* 70, 510 (1927).
5. F. Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, p. 74, Leipzig (1931).

## ISONITROSOACETYLACETONE

$C_5H_7O_3N$

Mol. Wt. 129.11

Beil. Ref. I, 807.



**Use:** Detection of iron.

Isonitrosoacetylacetone is a crystalline solid. It melts at 73° C. It is easily soluble in water and alcohol.

**Preparation:** Prepare a suspension of 50 g. of acetylacetone in 500 ml. of 7 per cent sulfuric acid, and add in a thin stream, and with shaking, a solution of 35 g. of sodium nitrite in 150 ml. of water. Extract the mixture with ether. Wash the extract with water and dry. Upon evaporation of the ether, the reagent separates as a crystalline mass. Recrystallize from ethyl acetate.<sup>1</sup>

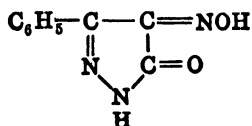
**Detection of iron.** Like other isonitroso compounds, isonitrosoacetylacetone gives a characteristic blue color with ferrous iron. The test is carried out by adding the reagent to the solution to be tested, and following with a few drops of ammonium hydroxide or sodium acetate. The test is sensitive to 0.0075 per cent ferrous iron.<sup>2</sup>

1. Wolff, *Ann.* **325**, 139 (1902).
2. W. Kuster, *Z. physiol. Chem.* **155**, 157 (1926).

**ISONITROSO-3-PHENYLPYRAZOLONE** $C_9H_7O_2N_3$ 

Mol. Wt. 189.15

Beil. Ref. XXIV, 390.

**Use:** Determination of copper.

Isonitroso-3-phenylpyrazolone is obtained as a yellow crystalline solid from water. This product melts at 188° C. Red needles are obtained by recrystallizing from acetic acid. This form melts at 184° C. This compound is soluble in alcohol and ether, and also dissolves in sodium hydroxide solutions to give a deep red color. The reagent acts as a strong acid.

**Preparation.** *3-Phenylpyrazolone:* Mix 50 g. of hydrazine hydrate and 192 g. of benzoylactic ester<sup>1</sup> and add 3 volumes of absolute alcohol. After the reaction has started, boil the mixture on a water-bath with reflux for one-half hour. Allow to stand until cool, and purify the crystalline mass by twice recrystallizing from alcohol.

*Isonitroso-3-phenylpyrazolone:* Isonitroso-3-phenylpyrazolone is prepared by passing the gaseous oxides of nitrogen into an aqueous suspension of 3-phenylpyrazolone. The mixture soon becomes red in color and dull yellow needles separate from the aqueous solution.<sup>2</sup>

**Determination of copper.** Isonitroso-3-phenylpyrazolone reacts with solutions of copper salts to form an insoluble microcrystalline, brownish-green copper compound of the following composition,  $Cu(C_9H_6N_3O_2)_2$ . Two methods of analysis are based on the formation of this compound.<sup>3</sup> One of these, the so-called tartrate method, is carried out as follows:

**Procedure.** Neutralize with ammonia the acid solution containing about 0.1 g. of copper as the sulfate, nitrate or chloride, and then add 5 ml. of 0.5 N sulfuric acid and 2.5-5.0 g. of ammonium tartrate. Dilute with water to 100-150 ml. and heat to 80° C. Add 85-90 ml. of a 1 per cent solution of isonitroso-3-phenylpyrazolone in 67 per cent methyl alcohol or in hot 50 per cent ethyl alcohol. The supernatant liquid above the precipitate should be yellowish-brown. Allow the mixture to stand overnight and filter through paper. Wash with cold 1-2 per cent ammonium tartrate solution and add oxalic acid to the moist precipitate. Ignite and weigh as  $CuO$ . This method can be used in the presence of considerable cadmium, aluminum, iron, lead, nickel and cobalt.<sup>4</sup>

The second method, the so-called acetate method, is carried out as described above, except for the following modifications: after neutralizing with ammonia



and making slightly acid with sulfuric acid, add 10-15 ml. of 10 per cent sodium acetate solution which has been made neutral to phenolphthalein.

1. L. Claisen and O. Lowman, *Ber.* 20, 653 (1887).
2. v. Rothenburg, *J. prakt. Chem.* [2] 52, 27 (1895).
3. V. Hovorka and J. Vorisek, *Chem. Listy.* 36, 73-8 (1942); *C.A.* 37, 4321 (1943).

#### 4-ISONITROSO-1-PHENYL-3-METHYLPYRAZOLONE-5

$C_{10}H_9O_2N_3$

Mol. Wt. 203.17    Beil. Ref. XXIV, 327(318).

**Use:** Detection of antimony, bismuth, cadmium, cobalt, copper, iron, lead, manganese, mercury, nickel, silver, uranium and zinc.

4-Isonitroso-1-phenyl-3-methylpyrazolone-5 is obtained as an orange crystalline solid by crystallizing from acetic acid or alcohol. It melts at 157° C. It is very slightly soluble in water, moderately soluble in ether and easily soluble in alcohol and hot acetic acid. It is only very slightly soluble in acids, but dissolves in alkalis with the formation of a yellowish-red color.

**Preparation.** *Isonitrosoacetic ester:* Dissolve 4.5 g. of acetoacetic ester in a solution prepared by dissolving 2.1 g. of potassium hydroxide in 80 ml. of water, and then add 2.5 g. of sodium nitrite dissolved in 10 ml. of water. Acidify the solution, make alkaline, and again acidify. Cool constantly during these operations. Extract the isonitrosoacetic ester with ether.

*4-Isonitroso-1-phenyl-3-methylpyrazolone-5:* This compound is prepared by heating an equal quantity of isonitrosoacetic ester and phenylhydrazine. The condensation is best carried out in a toluene or acetic acid solution. Purify the product by recrystallizing from hot acetic acid.<sup>1</sup>

The reagent may also be prepared by allowing a solution containing 2 parts of sodium nitrite to flow in gradually and with shaking into a cool hydrochloric acid solution containing 5 parts of phenylmethylpyrazolone. A reddish oil immediately separates, which by addition of a little ether may be made to crystallize. Purify the product by recrystallizing from hot acetic acid.<sup>2</sup>

**Reaction with metals.** Many cations react with 4-isonitroso-1-phenyl-3-methylpyrazolone-5 to form colored precipitates which may be used for the identification of the metals. The test may be made by adding a 1 per cent solution of the reagent in 50 per cent alcohol to acetate-buffered solutions of the sulfates, nitrates, perchlorates and acetates of the metals. The following compounds have been prepared and described by Hovorka and Sykora<sup>3,5</sup> and Dubsky, Brychta, and Kuras:<sup>4</sup>

(a) *Silver:* Silver yields a flocculent orange precipitate with 4-isonitroso-1-phenyl-3-methylpyrazolone-5 in buffered solutions.

(b) *Mercury:* Solutions of mercurous salts yield a voluminous orange-yellow precipitate, and mercuric compounds yield an orange precipitate.

(c) *Lead*: Lead salts yield a clear yellow precipitate in solutions which are well buffered.

(d) *Copper*: Cuprous salts give a brown precipitate, and cupric salts a clear green precipitate of  $\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2)_2$ .

(e) *Bismuth*: Bismuth gives a clear yellow precipitate, which readily dissolves in acetic acid.

(f) *Iron*: Ferric salts react with the reagent to give a red solution, and a red precipitate forms on the addition of a suitable buffer. A green colored solution is formed with ferrous salts, but no precipitate is obtained unless the concentration of iron is relatively high.

(g) *Manganese*: Manganese salts react with 4-isonitroso-1-phenyl-3-methylpyrazolone-5 to give a green precipitate of  $\text{Mn}(\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2)_2$ .

(h) *Nickel*: Nickel salts yield a clear green precipitate from buffered solutions.

(i) *Uranium*: Solutions of uranyl salts yield a reddish-orange precipitate of  $\text{UO}_2(\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2)_2$ , and precipitation is complete in well-buffered solutions.

(j) *Zinc*: Zinc salts yield a light yellow precipitate with the reagent.

(k) *Cadmium*: Cadmium forms a yellow precipitate from a solution buffered with sodium acetate.

(l) *Antimony*: Antimony salts yield orange precipitates from solutions buffered with sodium acetate.

(m) *Cobalt*: Cobalt salts yield yellowish-brown precipitates from solutions buffered with sodium acetate.

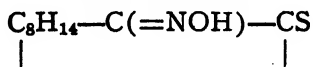
**Substituted pyrazolones.** Hovorka and Sykora<sup>5,6</sup> have studied a number of isonitroso-derivatives of pyrazolone, and have found their reactions similar to those of 4-isonitroso-1-phenyl-3-methylpyrazolone-5.

1. M. Ceresole, *Ber.* 15, 1326 (1882).
2. L. Knorr, *Ann.* 238, 158, 185.
3. V. Hovorka and V. Sykora, *Collection Czechoslov. Chem. Communications.* 11, 70-6 (1939); *C.A.* 33, 3287 (1939).
4. J. V. Dubsky, Fr. Brychta and M. Kuras, *Pub. faculte sci. univ. Masaryk.* 129, 1-26 (1931); *C.A.* 26, 2943 (1932).
5. V. Hovorka and V. Sykora, *Chem. Listy.* 35, 89-93 (1941); *C.A.* 37, 3023 (1943).
6. V. Hovorka and V. Sykora, *Chem. Listy.* 35, 170-5 (1941); *C.A.* 37, 3024 (1943).

## ISONITROSOTHIOCAMPHOR

$\text{C}_{10}\text{H}_{15}\text{ONS}$

Mol. Wt. 197.28



**Use:** Determination of cobalt.

Isonitrosothiocamphor is a violet crystalline solid. It melts at 148° C.

**Preparation:** *Thiocamphor:* Dissolve 30 g. of camphor in 150 ml. of absolute alcohol and cool to 0° C. Saturate with hydrogen chloride and hydrogen sulfide for 5-6 hours. Add 25 ml. of cold water and filter. Wash the residue and dissolve in benzene. Dry and evaporate to obtain thiocamphor.<sup>1</sup>

*Isonitrosothiocamphor:* Mix a solution of 17 g. of thiocamphor in 15 ml. of ether with 12 g. of isoamyl nitrite and cool to 0° C. Add this mixture gradually with stirring to an ice-cold solution of 4 g. sodamide in 7 ml. of anhydrous ether. Keep the mixture at 0° C. for 30 minutes, and then dilute and extract with ether. A violet crystalline precipitate of the reagent is obtained when dilute acetic acid is added to the aqueous layer.<sup>2,4</sup>

**Determination of cobalt.** From 0.01-0.04 g. of cobalt can be completely precipitated by adding a 1.0 per cent solution of isonitrosothiocamphor to a slightly acid solution of a cobalt salt. The scarlet precipitate which is formed contains only 9.0 per cent of cobalt, and corresponds to the formula,



The corresponding nickel compound is soluble in diluted hydrochloric acid, and this makes possible the determination of cobalt in the presence of nickel.<sup>3,4</sup>

**Procedure.** Dilute a solution of a cobalt salt containing not more than 0.04 g. of cobalt to 200 ml. with water, and heat to boiling. Add 50 ml. of 10 per cent sodium acetate solution and a 1.0 per cent isonitrosothiocamphor solution until precipitation is complete. Wash the precipitate with hot water to remove sodium acetate, then with 0.02 N sodium hydroxide to remove the excess reagent, and finally wash with 2 N hydrochloric acid and hot water. Dry at 105-110° C. and weigh. In the presence of nickel, add 30 ml. of 2 N hydrochloric acid after precipitating cobalt, and then filter the mixture after allowing to stand 30-40 minutes. The factor for cobalt is 0.0910.

Isonitrosothiocamphor possesses some advantages over  $\alpha$ -nitroso  $\beta$ -naphthol as a precipitant for small quantities of cobalt, due chiefly to its stability.

1. D. C. Sen, *J. Indian Chem. Soc.* 12, 647-52 (1935); *C.A.* 30, 1778 (1936).
2. D. C. Sen, *Sci. and Cult.* 4, 134-35.
3. D. C. Sen, *J. Indian Chem. Soc.* 15, 473-4 (1938); *C.A.* 33, 1622 (1939).
4. D. C. Sen, *J. Indian Chem. Soc.* 12, 751 (1935).

## ISONITROSOTHIOLGLYCOLIC ACID



Mol. Wt. 121.10

Beil. Ref. II, 564.



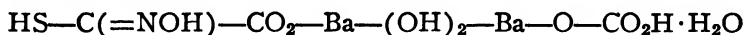
**Use:** Detection of iron.

**Preparation.** *Basic barium salt:* Mix 5 g. of isonitrosothiohydantoin with 100 ml. of water, and add gradually with constant mixing 30 g. of finely pow-

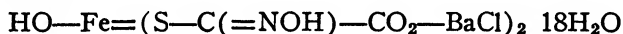
dered crystalline barium hydroxide. Shake thoroughly, place in a flask and fill with 100 ml. of water, and heat with constant shaking for 12 minutes. Cool with continuous shaking for 10 minutes under running water, and allow to stand for 15 minutes. Filter the yellow precipitate with suction, wash 4 times with filtered barium hydroxide solution, and dissolve in ice-cold, dilute hydrochloric acid. Filter and again precipitate with an excess of barium hydroxide. Dry 30 minutes on a porous plate, and then in a desiccator.

**Normal barium salt:** Add 3 g. of the basic barium salt to an ice-cold mixture of 20 ml. of water and 2 ml. of concentrated hydrochloric acid. Filter, cool the filtrate 10 minutes in ice, and then add gradually 7 ml. of ammonium hydroxide. Then again carefully acidify with constant cooling, and allow to stand for a few days. Filter off the precipitate and dry on a porous plate.<sup>1-3</sup>

**Detection of iron.** A dark blue ferric salt is prepared by treating 2 g. of the basic barium salt



with an acidified 0.1 N solution of ferric chloride until solution is complete. The ferric salt is precipitated by the addition of ethyl alcohol. The ferric compound corresponds to



Dubsky and Mareth<sup>1</sup> report that the blue color may be obtained with as little as 3γ of ferric iron at a concentration of 1:7,333,000.

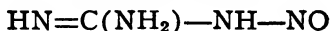
1. J. V. Dubsky and B. Mareth, *Mikrochem. ver. Mikrochim. Acta.* **29**, 213-18 (1941); *C.A.* **37**, 4320 (1943).
2. R. Maly and R. Andreasch, *Ber.* **13**, 602 (1880).
3. R. Maly, *Ber.* **12**, 967 (1879).

## NITROSOGUANIDINE



Mol. Wt. 88.04

Beil. Ref. III, 124(59).



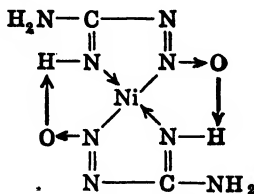
**Use:** Detection of copper, iron, nickel and silver.

Nitrosoguanidine is a yellow crystalline solid. It explodes without melting at 160-165° C. It is insoluble in alcohol and ether, but is slightly soluble in cold water and more easily in hot water.

**Preparation.** Mix 30 g. of nitroguanidine with 500 ml. of water and add 100 g. of zinc, and then add a cooled mixture of 10 ml. of sulfuric acid and 50 ml. of water. The temperature of the mixture rises to 40-50° C., but should be prevented from rising higher by cooling with ice. After about 5-10 minutes the nitro-compound disappears, and a gray-yellow precipitate is formed. Filter with suction and extract the residue on the filter several times with hot but not boiling water until the drop of water which cools on the stem of the funnel is no longer yellow in color. About 1-1.5 liters of water is needed. Cool the

filtrate and the wash water to 0° C. and allow to stand for several hours in ice. The nitrosoguanidine separates as a crystalline solid.<sup>1</sup>

**Reactions with the metals.** Very dilute nickel solutions react with nitrosoguanidine on the addition of sodium acetate to give a beautiful brick-red, flocculent precipitate of  $\text{Ni}(\text{CH}_3\text{N}_4\text{O})_2$ , which is soluble in ammonia. This compound has been assigned the following formula:



A white flocculent precipitate of  $\text{Ag}(\text{CH}_3\text{N}_4\text{O})$  is formed when an aqueous solution of nitrosoguanidine is mixed with an ammoniacal solution of a silver salt.

A reddish-brown precipitate of  $\text{Cu}(\text{CH}_3\text{N}_4\text{O})_2$  is formed when an aqueous solution of nitrosoguanidine is mixed with an ammoniacal solution of a cupric salt. A dilute solution of nitrosoguanidine reacts with ferrous salts in an alkaline solution to form a purple color.<sup>1</sup>

1. J. Thiele, *Ann.* 273, 133 (1893).

## TRINITROSOPROPANE

$\text{C}_3\text{H}_5\text{O}_3\text{N}_3$

Mol. Wt. 131.07

Beil. Ref. I-806.



**Use:** Detection of cadmium, cobalt, copper, iron, lead and nickel.

Trinitrosopropane is obtained as a colorless crystalline compound from water. It melts at 171° C. It is slowly but markedly soluble in hot water, readily soluble in alcohol, and only slightly soluble in ether.

**Preparation.** Warm dinitrosoacetone (for preparation, see page 277) with 7-8 times as much water and an equal molecular quantity of hydroxylamine hydrochloride and sodium acetate for 1-2 hours at 50-60° C. Allow to stand for several hours and collect the reagent which separates from the liquid as a brown crystalline solid. Purify the crude product by recrystallizing several times from hot water, the last time with a little animal charcoal.

**Reactions.** When a solution of sodium carbonate is added dropwise to an aqueous solution of trinitrosopropane and copper sulfate, a green, explosive powder is formed. In a similar manner a black-violet ferrous salt is obtained by substituting ferrous ammonium sulfate for copper sulfate in the above procedure. With ferric chloride and ammonia, trinitrosopropane forms a brown crystalline compound. When a solution of sodium carbonate is added to an

aqueous solution of nickel chloride and trinitrosopropane a red compound is formed. By substituting cobalt chloride for nickel chloride an analogous compound is formed. This compound is dark brown in color.

Lead acetate yields white needles, and cadmium sulfate with ammonia gives a yellow turbidity.<sup>2</sup>

1. H. v. Pechmann and K. Wehsarg. *Ber.* 21, 2991 (1888).
2. J. V. Dubsky, Fr. Brychta, and M. Kuras, *Pub. faculte sci. univ. Masaryk.* 129, 1-26 (1931); *C.A.* 26, 2943 (1932).

## VIOLURIC ACID

Synonym: 5-Isonitrosobarbituric acid, alloxanoxime-5, 5-nitroso-2,4,6-trihydroxypyrimidine

$C_4H_3O_4N_3$

Mol. Wt. 157.09

Beil. Ref. XXIV, 506.



**Use:** Detection of ammonium, barium, calcium, copper, lead, magnesium, mercury, potassium, sodium and strontium.

Violuric acid is a crystalline solid which is only sparingly soluble in water, to which it imparts a violet color. It is soluble in alcohol.

**Preparation.** Place a suspension of 5 g. of uric acid in 22 ml. of hydrochloric acid ( $d = 1.06$ ), and gradually add at  $45^\circ C$ . 1.2 g. of potassium chlorate. Pass a stream of air through the solution to remove excess chlorine, and then warm with 1.5 moles of hydroxylamine hydrochloride on a hot, but not boiling water-bath. After two hours allow to cool and add a solution of barium hydroxide until the mixture is alkaline. Precipitate the excess barium with carbon dioxide and heat to boiling, and then filter while hot. A violet crystalline precipitate separates from the filtrate on cooling. Filter, wash with cold water, and convert the barium salt to the free acid with sulfuric acid.<sup>1-3</sup>

**Chromatographic analysis.** Various investigators<sup>4-7</sup> have observed that violuric acid reacts with metallic salts to give colored compounds. The colors of a number of these compounds are given in Table 50.

TABLE 50.

Metal	Color	Metal	Color
Lithium	Light carmine-red	Calcium	Red
Sodium	Red	Strontium	Red
Potassium	Blue	Barium	Red
Rubidium	Blue	Lead	Dark-red
Cesium	Blue	Zinc	Carmine-red
Ammonium	Blue-violet	Cadmium	Red-brown
Beryllium	Dark-red	Thallium	Red
Magnesium	Carmine-red	Silver	Green

Erlenmeyer and co-workers<sup>8,9</sup> have used violuric acid alone, or mixed with diatomaceous earth, barium sulfate or starch to fill adsorption columns in chromatographic analysis. With this reagent, and employing the chromatographic technique, it has been found possible to distinguish between the elements in various pairs. A tube 3 mm. x 40 mm. was used, and to form well defined zones it was found necessary to dissolve the salts in acetic acid solutions. The results obtained with various pairs of elements are given in Table 51.

TABLE 51.

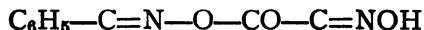
Mixture	Zone 1	Zone 2	Separation
Potassium-sodium	Potassium-violet	Sodium-red-violet	Good
Ammonium-sodium	Ammonium-violet	Sodium-red-violet	Good
Potassium-ammonium	Potassium-violet	Ammonium-violet	Poor
Potassium-magnesium	Potassium-violet	Magnesium-brick-red	Good
Magnesium-sodium	Magnesium-brick-red	Sodium-red-violet	Fair
Ammonium-magnesium	Ammonium-violet	Magnesium-brick-red	Good
Barium-calcium	Barium-violet-red	Calcium-red	Good
Barium-strontium	Barium-violet-red	Strontium-violet-red	Poor
Strontium-calcium	Strontium-violet-red	Calcium-red	Good
Copper-mercuric	Copper-green	Mercuric yellow	Good
Lead-mercuric	Lead-brown	Mercuric yellow	Good
Copper-lead	Copper-green	Lead-brown	Good

1. R. Andreasch, *Monatsh.* 21, 281-300 (1900).
2. M. Ceresole, *Ber.* 16, 1133 (1883).
3. A. v. Baeyer, *Ann.* 130, 140 (1864).
4. A. v. Baeyer, *Ann.* 127, 200 (1863).
5. A. Hantzsch and Isherwood, *Ber.* 42, 986-1000 (1909).
6. J. Wagner, *Z. physikal. Chem.* 12, 314 (1893).
7. A. Hantzsch and B. Issaias, *Ber.* 42, 1000-07 (1909).
8. H. Erlenmeyer and W. Schoenauer, *Helv. Chim. Acta.* 24, 878-9 (1941); *C.A.* 36, 2221 (1942).
9. H. Erlenmeyer and J. Schmidlin, *Helv. Chim. Acta.* 24, 1213-18 (1941); *C.A.* 36, 3451 (1942).

### 5-OXO-4-OXIMO-3-PHENYLISOXAZOLIN



Mol. Wt. 190.14



**Use:** Detection and determination of potassium and sodium.

**Preparation.** *Phenylisoxazonol*: Dissolve 1 mole of benzoyl acetic ester in 8-9 times as much acetic acid and add 1 mole of finely powdered hydroxylamine hydrochloride. Warm on a water-bath until all of the hydroxylamine hydrochloride has dissolved and then boil for 30 minutes. The greater part of the acetic acid is volatilized during the boiling and the remainder is removed by

evaporation on a water-bath. Allow the mixture to stand until cool. Separate the brown mass which forms, dry on a porous plate, and finally purify from boiling alcohol.

**5-Oxo-4-oximo-3-phenylisoxazolin:** Dissolve a few grams of phenylisoxazolon in a little more than the calculated quantity of 1 N sodium hydroxide and add an excess of sodium nitrite. Allow this mixture to drop into cooled, dilute sulfuric acid. The reagent separates as a voluminous, light yellow precipitate. This is filtered, washed and crystallized from boiling water.<sup>1</sup>

**Determination of sodium and potassium.** 5-Oxo-4-oximo-3-phenylisoxazolin is used to replace violuric acid in the chromatographic analysis of mixtures of sodium and potassium. The reagent consists of a 1:2 5-oxo-4-oximo-3-phenylisoxazolin-starch mixture, which is contained in an adsorption tube measuring 2.5 x 50 mm. Potassium acetate is indicated by a yellow zone and sodium acetate by a red zone. The quantity of sodium and potassium is indicated by the length of the zone of coloration.<sup>2</sup>

1. L. Claisen and W. Zedel, *Ber.* **24**, 140 (1891).
2. H. Erlenmeyer and J. Schmidlin, *Helv. Chim. Acta.* **24**, 1213-18 (1941); *C.A.* **36**, 3451 (1942).



## CHAPTER XI

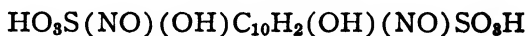
### NITROSO PHENOLS

#### CHROMOTROPIC ACID DIOXIME

Synonym: 2,7-Dinitroso-1,8-dihydroxynaphthalene-3,6-disulfonic acid

$C_{10}H_8O_{10}N_2S_2$

Mol. Wt. 378.27



**Use:** Detection of cobalt, copper and nickel.

**Preparation:** Dissolve 10 g. of chromotropic acid in 300 ml. of boiling distilled water, which contains 50 ml. of 5 N acetic acid. Cool to 15° C. and slowly add 5 g. of sodium nitrite while cooling with water to 10-15° C. Allow to stand for 5 minutes and add 50 ml. of piperidine and then dilute the solution to 2 liters with distilled water. The reagent used in the test for cobalt, nickel and copper is prepared by diluting 10-20 ml. of this solution to 300 ml. with distilled water.

**Detection of cobalt, copper and nickel.** In the presence of only traces of cobalt, the brown-yellow color of a slightly ammoniacal 1:5,000 solution of chromotropic acid dioxime changes to a corn-flower-blue. Nickel changes the color to violet, and copper to a violet-blue. Only the color caused by cobalt, however, remains upon the addition of potassium cyanide. Copper and nickel can be distinguished from one another in the absence of cobalt, since the copper (but not nickel) reaction is inhibited by thiosulfates, and the nickel (but not copper) reaction is inhibited by ammonium thiocyanate.

The following test for cobalt has been proposed by Steigmann:<sup>1</sup>

**Procedure.** Add 0.1-0.2 ml. of the reagent described above to 0.5-1.0 of a faintly acid or neutral solution to be tested (pH = 5.5-7.0) in a narrow test tube. The test may be carried out as a drop reaction by adding a drop of a 1:1,000 solution of the reagent to a drop of the solution to be tested on a spot plate. A blank test with water is carried out at the same time. When 0.1-0.2 ml. of an 0.5 per cent potassium cyanide solution is added to the test tube, or a drop of 0.5 per cent potassium cyanide to the spot plate, a blue or blue-violet color forms if cobalt is present.

The color is best observed in the test tube reaction if, before adding the cyanide, sufficient dilute acetic acid is added to reverse the color change, followed by just sufficient dilute piperidine to restore it to the original color. In a test tube reaction this test is sensitive to 1:3,000,000, and by means of a drop reaction as little as 0.05-0.1γ of cobalt can be detected.

Other metals do not interfere with this reaction at ordinary temperatures, but palladium gives a dark violet color upon heating.

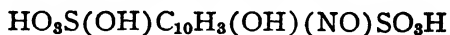
1. A. Steigmann, *J. Soc. Chem. Ind.* **62**, 42-3 (1943); *C.A.* **37**, 3689 (1943).

**1,8-DIHYDROXY-2-NITROSO-3,6-NAPHTHALENE  
DISULFONIC ACID**

Synonym: Nitrosochromotropic acid

$C_{10}H_7O_9NS_2$

Mol. Wt. 349.28



**Use:** Determination of cobalt, copper and nickel.

**Preparation:** For analytical use, nitrosochromotropic acid is not prepared in the pure state and isolated, but rather it is formed directly from chromotropic acid, and is used in the form of a solution. The method for preparing the solution will be given in the following sections:

**Determination of copper.** Cupric ions in an ammoniacal solution react with various *o*-nitrosohydroxy aromatic derivatives to form intensely colored lakes having a color different from that of the dye. Among this group is nitrosochromotropic acid, which forms with ammoniacal solutions of copper salts a compound of intense permanganate color. This appears to be caused by the union of one cupric ion with two molecules of the nitrosochromotropic acid.

When an excess of the yellowish-brown nitroso dye is added to the solution containing the copper salt, the permanganate color changes to brown. This color change may serve as an indicator, thus making possible the titration of very small amounts of copper with an accuracy of approximately 0.5%. This method, which has been developed by Ansbacher, Remington, and Culp,<sup>1</sup> may be carried out as follows:

**Preparation of reagent.** Dissolve 0.37 g. (0.001 mole) of the sodium salt of chromotropic acid in a small quantity of water, and add 1 ml. of 2 N sodium carbonate, 0.5-0.6 ml. of 2 N sodium nitrite, and a slight excess of dilute acetic acid. Allow the mixture to stand 24 hours, filter, and make weakly alkaline with sodium carbonate. Dilute with water to 100 ml. (0.01 N), and to 34 ml. of this solution add 50 ml. alcohol and dilute with water to 1 liter. One ml. of this solution is equivalent to about 10% of copper.

**Standardization of reagent.** Dissolve 2.5 g. of crystalline copper sulfate in 250 ml. of water and determine the copper content electrolytically in a 25-ml. aliquot. Dilute a 10-ml. aliquot to 250 ml. One ml. of this solution contains approximately 49.1% of copper. This value should be expressed exactly for the determination.

Place exactly 1 ml. of the standard copper solution in a test tube, add 3 drops of concentrated ammonia, and then add the reagent dropwise from a buret until the permanganate color changes to brown. The titration should be carried out in pure daylight. Near the end point, add only parts of drops. If 1 ml. of

the standard copper solution requires, say 7.32 ml. of reagent, the titer of the solution is determined as follows

$$\frac{49.1 \text{ (copper content of 1 ml. standard solution in } \gamma)}{7.32 \text{ (number ml. reagent solution)}} = 6.7\gamma \text{ copper}$$

**Procedure.** Pipet an aliquot of the neutral solution to be analyzed into a test tube and add 3 drops of concentrated ammonia. Run in the nitrosochromotropic acid reagent from a buret, as in the standardization procedure, until the end point is reached. From the number of ml. of solution used in the titration, calculate the copper content of the unknown in  $\gamma$ .

This method may be used to estimate quantities of copper as low as 2.3 $\gamma$  with an accuracy of 0.5 $\gamma$ . The chief difficulty in this procedure lies in the ability of the operator to recognize the end point; some practice is required to achieve satisfactory results.

The method for determining small quantities of copper appears to be adaptable to a wide variety of biological materials.<sup>2-7</sup> For the most part results are claimed to be excellent,<sup>2</sup> although in a few instances unsatisfactory results have been reported.<sup>8</sup>

**Determination of cobalt and nickel.** Like copper, cobalt in ammoniacal solutions reacts with nitrosochromotropic acid to give a dark blue color with as little as 0.001 mg. of cobalt per ml. It has not been possible to develop a colorimetric method for cobalt based upon the formation of this color, but as with copper, an application of the principle of microtitration has given satisfactory results. The following method may be used with an accuracy of 5 per cent for concentrations of cobalt as low as 0.001 mg. per ml.:<sup>8</sup>

**Reagent.** Treat 0.37 g. of chromotropic acid with 1 ml. of 2 N sodium hydroxide, 0.5 ml. of 2 N sodium nitrite, and a slight excess of dilute acetic acid. Allow to stand 24 hours, filter, and dilute with water to 100 ml. This makes a 0.01 N solution. Dilute 6.8 ml. of this solution to 200 ml. One ml. of this solution is equivalent to 0.01 mg. of cobalt. Standardize against a solution of cobalt chloride of known strength as described in the method for determining copper.

**Procedure.** Dissolve in 10 ml. of water a sample containing approximately 0.01 g. of cobalt, and add a few drops of concentrated ammonia and a little sodium acetate. Then titrate this solution with the reagent until the color of the solution changes from blue to red.

This method may also be used for the microtitration of nickel.

1. S. Ansbacher, R. E. Remington, and F. B. Culp, *Ind. Eng. Chem., Anal. Ed.* **3**, 314-7 (1931); *C.A.* **25**, 5112 (1931).
2. O. Sheets, R. W. Pearson, M. Gieger, *Ind. Eng. Chem., Anal. Ed.* **7**, 109-10 (1935); *C.A.* **29**, 2879 (1935).
3. L. W. Conn, A. H. Johnson, H. H. Trebler, and V. Karpenko, *Ind. Eng. Chem., Anal. Ed.* **7**, 15-23 (1935); *C.A.* **29**, 1523 (1935).
4. S. Ansbacher, *Etude de Chimiotherapie de la Tuberculose*, pp. 26-35, Geneva, Imprimerie Kundig (1933).

5. E. Cherbuliez and S. Ansbacher, *Arch. path. Anat. (Virchow's)*, **276**, 365 (1930).
6. E. Cherbuliez and S. Ansbacher, *Helv. Chim. Acta*, **13**, 187 (1930); *C.A.* **24**, 2402 (1930).
7. M. A. Ohlson and K. Daum, *J. Nutrition*, **9**, 75 (1935).
8. C. Brenner, *Helv. Chim. Acta*, **3**, 90-103 (1920); *C.A.* **14**, 1271 (1920).

**DINITROSOORCINOL**      Synonym: 2,4-Dinitroso-3,5-dihydroxytoluene  
 $C_7H_6O_4N_2$       Mol. Wt. 182.12      Beil. Ref. VII, 887 (490).  
 $(NO)_2C_6H(CH_3)(OH)_2$

**Use:** Determination of cobalt.

Dinitrosoorcinol is a yellow, crystalline solid. It darkens at 110° C. without melting. It is almost insoluble in water, alcohol, ether and benzene, but is soluble in hot acetic acid.

**Preparation:** Dissolve 7 g. of orcinol and 7 g. of sodium nitrite in 50 ml. of water, and allow this solution to drop slowly into a cooled mixture of 10 g. of concentrated sulfuric acid and 500 ml. of water. Allow to stand 30 minutes and filter the separated solid with suction. Wash with water.<sup>1</sup>

**Determination of cobalt.** Cobalt may be determined gravimetrically by precipitating as  $Co(C_7H_5O_4N_2)_2$  with dinitrosoorcinol.<sup>2</sup> Good results are obtained, although it is difficult to wash the precipitate free from adsorbed reagent.

**Reagent.** Dissolve 1 g. of dinitrosoorcinol in 100 ml. glacial acetic acid and dilute to 500 ml.

**Procedure.** Heat the solution containing 10-40 mg. of cobalt to boiling, and add a slight excess of the reagent. Allow the mixture to stand for 20 minutes and filter, using slight suction. Wash the precipitate with 15 per cent acetic acid and dry at 115° C. for 2-3 hours.

1. F. Henrich, *Ber.* **37**, 1412 (1904).
2. S. S. Guha-Sircar and S. C. Bhattacharjee, *J. Indian Chem. Soc.* **18**, 155-60, 161-3 (1941); *C.A.* **35**, 7869 (1941).

**DINITROSORESORCINOL**      Synonym: 2,4-Dinitroso-1,3-dihydroxybenzene  
 $C_6H_4O_4N_2$       Mol. Wt. 168.09      Beil. Ref. VII, 885 (490).  
 $(NO)_2C_6H_2(OH)_2$

**Use:** Detection of cobalt, copper and iron.

Determination of cobalt, copper.

Dinitrosoresorcinol is obtained as yellowish-gray or yellowish-brown leaves from 50 per cent alcohol. It is slightly soluble in cold water or alcohol, but it is insoluble in ether and benzene.

Results obtained using the same method, but in the presence of 0.06 g. of nickel are shown in Table 53.

TABLE 53.—DETERMINATION OF COBALT  
(0.06 g. Nickel)

Cobalt Taken g.	Precipitate g.	Cobalt Found g.	Error mg.
0.0043	0.0294	0.0044	+0.1
0.0217	0.1432	0.0215	-0.2
0.0217	0.1440	0.0216	-0.1
0.0217	0.1444	0.0217	0.0
0.0217	0.1427	0.0214	-0.3

Cobalt can be determined in the presence of nickel, but it is necessary to wash the precipitate with 50 ml. of 0.085 N hydrochloric acid to remove the nickel. Cobalt can also be determined in the presence of manganese, but copper and iron must be removed.

Guha-Sircar and Bhattacharjee<sup>7</sup> claim that the precipitate obtained with dinitrosoresorcinol is washed free of adsorbed reagents only with difficulty. They have used a somewhat different procedure:

**Procedure.** To a boiling solution containing 10-40 mg. of cobalt, add a slight excess of a solution prepared by dissolving 1 g. of dinitrosoresorcinol in 100 ml. of glacial acetic acid and diluting to 500 ml. Digest for 20 minutes, filter with slight suction, wash with 15 per cent acetic acid and dry at 115° C. for 2-3 hours.

Tomicek and Komarek<sup>4,6</sup> have studied the method of Orndorff and Nichols, and report that precipitation of cobalt with dinitrosoresorcinol is not quantitative, and that the apparently satisfactory results obtained with this method probably are due to a balancing of errors. They claim that the precipitate may contain as low as 80 per cent cobalt dinitrosoresorcinol, and that the remaining 20 per cent is free dinitrosoresorcinol and adsorbed salts, such as sodium acetate.

**Detection of copper, iron, and cobalt.** In a neutral solution, dinitrosoresorcinol reacts with copper, iron, and cobalt salts to yield colorations by means of which these metals may be identified. The reagent is prepared by adding an excess of dinitrosoresorcinol to boiling water and filtering. The clear filtrate is the reagent, and should be used soon after its preparation. Results obtained with this reagent are shown in Table 54.

TABLE 54.

Metal	Color	Sensitiveness
Copper	Brown	0.004 mg. per ml.
Iron	Olive-green	0.0035 mg. per ml.
Cobalt	Orange-brown	0.0033 mg. per ml.

Chromium and nickel may interfere with these tests. Wenger and co-workers<sup>10</sup> do not recommend the use of dinitrosoresorcinol for the detection of cobalt, since the same reaction is obtained with other ions of the same analytical group.

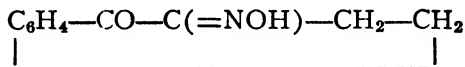
The use of dinitrosoresorcinol for the colorimetric determination of copper has also been studied,<sup>8</sup> but the reagent does not appear to offer any special advantages.

1. A. Fitz, *Ber.* **8**, 631 (1875).
2. W. R. Orndorff and M. L. Nichols, *J. Am. Chem. Soc.* **45**, 1536 (1923).
3. W. R. Orndorff and M. L. Nichols, *J. Am. Chem. Soc.* **45**, 1439-44 (1923); *C.A.* **17**, 2251 (1923).
4. O. Tomicek and K. Komarek, *Chem. Listy.* **26**, 515-20 (1932); *C.A.* **27**, 680 (1932).
5. M. L. Nichols and S. R. Cooper, *J. Am. Chem. Soc.* **47**, 1268 (1925); *C.A.* **19**, 1833 (1925).
6. O. Tomicek and K. Komarek, *Z. anal. Chem.* **91**, 90 (1932).
7. S. S. Guha-Sircar and S. C. Bhattacharjee, *J. Indian Chem. Soc.* **18**, 155-60, 161-3 (1941); *C.A.* **35**, 7869 (1941).
8. R. H. Muller and A. T. Burtzell, *Mikrochem. ver. Mikrochim. Acta.* **28**, 209-28 (1940); *C.A.* **34**, 7776 (1940).
9. J. V. Dubsy and A. Langer, *Chem. Obsor.* **12**, 27-32 (1937); *C.A.* **32**, 5326 (1938).
10. P. Wenger, R. Duckert and M. L. Busset, *Helv. Chim. Acta.* **24**, 657-70 (1941); *C.A.* **35**, 6536 (1941).

## 2-ISONITROSO-1-KETOTETRALIN

$C_{10}H_9O_2N$

Mol. Wt. 175.17



**Use:** Detection of cobalt.

2-Isonitroso-1-ketotetralin reacts with solutions of cobalt salts in much the same manner as the nitrosonaphthols, and consequently may be used for the detection of cobalt.<sup>1-3</sup>

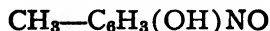
1. F. Strauss and W. Ekkard, *Ann.* **444**, 154 (1924).
2. F. Feigl, *Ind. Eng. Chem., Anal. Ed.* **8**, 403 (1936).
3. L. A. Sarver, *J. Chem. Ed.* **13**, 511-4 (1936); *C.A.* **31**, 334 (1937).

## *o*-NITROSOCRESOL

Synonym: 1-Methyl-3-hydroxy-4-nitrosobenzene

$C_7H_7O_2N$

Mol. Wt. 137.13



**Use:** Determination of cobalt.

Like *o*-nitrosophenol, this reagent is prepared for use in the form of a stock solution of the cupric salt. The method of preparation of this solution is described below in the section on reagents used for the cobalt determination.

**Determination of cobalt.** Ellis and Thompson<sup>1</sup> have described a quantitative colorimetric procedure for the determination of from 0.02 to 25 $\gamma$  of

cobalt in plant and animal tissues. This method depends on the formation of the colored complex of cobalt with *o*-nitrosocresol, the extraction of this compound with ligroin, and subsequent measurement of the ligroin solution in a photoelectric colorimeter. Iron, which may interfere in this determination, is completely separated from cobalt by use of dithizone or sodium diethyldithiocarbamate. Beer's law applies over a wide range of concentration, and the complex is stable for several days.

This reagent is reported to be more satisfactory than *o*-nitrosophenol, since it is more readily prepared in large quantities and produces a more intense color with cobalt.

The following procedure is recommended for the determination of cobalt in plant and animal tissues:

**Reagents.** *Stock solution of cupric o-nitrosocresol:* Dissolve exactly 6 g. of hydroxylamine hydrochloride and 15 g. of cupric chloride in 900 ml. of distilled water, and add 5 ml. of *m*-cresol. Add 15 ml. of 30 per cent hydrogen peroxide with stirring, and allow the mixture to stand 2 hours at room temperature. Then add 25 ml. of concentrated hydrochloric acid and shake with petroleum ether in a separatory funnel. Repeat the extraction with successive portions of petroleum ether until all the reagent is extracted. Wash the petroleum ether extract several times with distilled water, and then shake with several successive 50- to 100-ml. portions of 1 per cent aqueous cupric acetate solution until the petroleum ether layer is colorless. Approximately 400 ml. of a deep red solution of the cupric complex is obtained. Filter and store in a refrigerator. This solution is stable for several months.

*Sodium borate buffer:* Dissolve 20 g. of boric acid in 1 liter of redistilled water, and add 22.8 ml. of 1.0 N sodium hydroxide solution to adjust the pH to 7.7-7.8.

*Sodium o-nitrosocresol solution:* Transfer 75 ml. of the stock cupric *o*-nitrosocresol solution to a separatory funnel and add 10 ml. of concentrated hydrochloric acid, and then shake with 300-500 ml. of petroleum ether. Remove the aqueous layer and shake the petroleum ether solution with 2 successive 100-ml. portions of 0.01 N hydrochloric acid, and then with two 100-ml. portions of redistilled water. To the washed petroleum ether solution, add 25-ml. portions of a sodium borate buffer prepared by adding 20 ml. of 1.0 N sodium hydroxide to 1 liter of the borate buffer described above. Shake well and remove the buffer solution, and then repeat the treatment until the petroleum ether solution is almost colorless. The aqueous solution of the reagent may be kept about 1 month with refrigeration.

*Dithizone solution:* Dissolve 0.5 g. of dithizone in 600-700 ml. of carbon tetrachloride, and filter into a separatory funnel containing 2.5-3.0 liters of 0.02 N ammonium hydroxide. Shake well and discard the carbon tetrachloride layer. Shake the aqueous solution with 50-ml. portions of carbon tetrachloride until the carbon tetrachloride has a pure green color as it separates. Add 1 liter of carbon tetrachloride and acidify the mixture slightly with hydrochloric acid.



Again shake and separate the carbon tetrachloride layer. Store in a cool, dark place.

*Hydroxylamine-acetate buffer:* Dissolve 10 g. of hydroxylamine hydrochloride and 9.5 g. of anhydrous sodium acetate in 500 ml. of redistilled water. The pH of the solution should lie between 5.0-5.2.

*Potassium nitrate solution:* Purify a 5 per cent solution of potassium nitrate by shaking several times with a 0.1 per cent aqueous solution of sodium diethyldithiocarbamate and with carbon tetrachloride.

*Ammonium citrate solution:* Dissolve 800 g. of lead-free citric acid in 600 ml. of distilled water, and then add slowly with stirring 900 ml. of concentrated ammonium hydroxide. Adjust the pH to 8.5 if necessary. Dilute to 2 liters, and extract with 10-ml. portions of dithizone in carbon tetrachloride until the aqueous phase remains orange colored. Then extract the solution with carbon tetrachloride until the orange color disappears.

*Ligroin:* Distill ligroin (B.P. 70-90° C.) over dilute alkaline permanganate, and wash by shaking vigorously 3 times with distilled water in a separatory funnel.

**Procedure.** Dry-ash the material at 450-650° C. in a silica dish overnight. If the ashing is not complete, add 10 ml. of 1:1 nitric acid and 1 ml. of the purified potassium nitrate solution and evaporate to dryness, and then again ash, this time at 600-650° C. Repeat the nitric acid treatment if necessary. If the sample is high in silica, ash in platinum dishes, treat with 4 ml. of 48 per cent hydrofluoric acid and 1 ml. of perchloric acid, and evaporate to dryness. Dissolve the ash by heating with 1:1 hydrochloric acid. If the silica concentration is low, simply heat the hydrochloric acid solution of the ash several hours before neutralizing.

To separate cobalt from iron, transfer the sample solution to a separatory funnel and add 1 ml. of ammonium citrate solution for each g. of the dry tissue. Adjust the pH to 8.5 with ammonium hydroxide, using phenolphthalein as an internal indicator. Formation of a precipitate may be prevented by adding more ammonium citrate. Now add 10 ml. of the dithizone solution and shake vigorously for 30 seconds. Draw off the carbon tetrachloride and carefully collect in a beaker. Repeat the extractions with additional portions of dithizone solution until the original green color of the dithizone solution remains unchanged, and add to the original extract in the beaker. Evaporate the carbon tetrachloride extracts to dryness.

Add 2 ml. of perchloric acid to the residue in the beaker, cover with a watch glass, and boil until the mixture is colorless. Remove the cover and expel all perchloric acid by evaporation. Dissolve the residue in 5 ml. of 0.01 N hydrochloric acid and add 5 ml. of the sodium borate buffer. Transfer the solution to a 60-ml. separatory funnel and add the sodium *o*-nitrosocresol solution dropwise until all copper present has reacted. This point is determined by the appearance of an orange color, which is easily distinguished from the pink color of the copper complex. Then add an additional 1 ml. of the reagent in excess. Add

a measured volume of ligroin, usually 4-5 ml., depending on the amount of cobalt present, and shake the mixture for 5 minutes. Remove the aqueous layer, and to the ligroin solution add 5 ml. of a 1 per cent cupric acetate solution. Shake 1 minute and again remove the aqueous layer. Wash the ligroin, first with distilled water, and then with 5 ml. of the hydroxylamine-acetate buffer. Shake and remove the aqueous layer in each case. Unless large quantities of cobalt are present, the ligroin solution will remain colorless, since the light absorption of the cobalt *o*-nitrosocresol complex occurs in the near ultra-violet.

Transfer the ligroin solution to a 5- or 10-cm. absorption tube and read in a photoelectric colorimeter. Use corning standard thickness filters 5860 and 4308, or a light band as close as possible to the point of maximum absorption at 360  $\mu$ .

With samples containing a few hundredths  $\gamma$  of cobalt, deviations of the results from the mean may be as high as 10 per cent, while the per cent recovery ranges from 96 to 107. With samples containing a few tenths  $\gamma$  of cobalt, the results do not deviate from the mean by more than 3 per cent, while the percentage recovery ranges from 89 to 104.5. The average recovery is 97.4 per cent in the samples analyzed.

1. G. H. Ellis and J. F. Thompson, *Ind. Eng. Chem., Anal. Ed.* 17, 254-257 (1945).

### $\alpha$ -NITROSO- $\beta$ -NAPHTHOL

Synonym: 1-Nitroso-2-naphthol

$C_{10}H_7O_2N$

Mol. Wt. 173.16

Beil. Ref. VII-712.

$C_{10}H_8(OH)NO$

**Use:** Detection of boron, cobalt, copper, iron, molybdenum, nickel, palladium, vanadium and zirconium.

Determination of cobalt, copper, iron, palladium, potassium and zirconium.

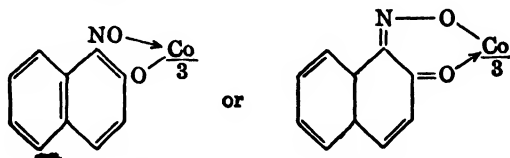
$\alpha$ -Nitroso- $\beta$ -naphthol consists of orange-brown crystals or a brown powder. It melts at 108-110° C. It dissolves in 1000 parts of water or 35 parts of alcohol, but it is freely soluble in a hot alcohol, benzene, ether, carbon disulfide, sodium or potassium hydroxide solutions and glacial acetic acid.

**Preparation:** Dissolve 14.4 g. of  $\beta$ -naphthol and 4 g. of sodium hydroxide in 200 ml. of water, using heat if necessary. Cool the mixture to 0° C. and add 6.9 g. of sodium nitrite. Again cool to 0° C. and allow 40 per cent sulfuric acid to drop in slowly and with constant stirring. A black tarry substance forms if the temperature rises above 3° C., but this can be prevented by the addition of small pieces of ice to the reaction mixture. Allow the sulfuric acid to drop into the solution until acid to congo-red paper. This requires about 30 ml. of the diluted acid. Allow the mixture to stand for about 15-20 minutes after all the sulfuric acid has been added, and keep cold during this interval. The mixture is light yellow in color and is of the consistency of ice cream.

Filter the heavy yellow precipitate with suction and wash well with water, and then dry with suction. Remove the residue from the funnel and allow

to dry in air by spreading out in a thin layer in a crystallizing dish. Four or five days are required for the drying process, but the product may be used while still damp.<sup>1,2</sup>

**Determination of cobalt.** *Gravimetric determination:*  $\alpha$ -Nitroso- $\beta$ -naphthol exists in two isomeric forms which react with cobalt salts to form inner-complex compounds of the following composition



The purple-red cobaltic salt is insoluble in acids, but is successfully precipitated only from a weakly acid, neutral, or ammoniacal solution, since the cobaltic salt is derived from the tautomeric quinoxime form of the reagent. Both forms exist together in equilibrium, but in strongly acid solution the equilibrium shifts to the phenol form; on the other hand, the quinoxime form predominates in a weakly acid solution.

Ilinski and v. Knorre first observed that  $\alpha$ -nitroso- $\beta$ -naphthol reacts with solutions of cobalt salts to form a brick-red precipitate, and in a series of investigations beginning in 1883 they published a number of important papers on the use of this reaction for the detection and the determination of cobalt.<sup>3-8</sup> Since then  $\alpha$ -nitroso- $\beta$ -naphthol has been widely studied and recommended as one of the most satisfactory reagents for cobalt.<sup>9-15,17-20,26-28</sup>

The composition of the precipitate formed in the reaction between cobalt salts and  $\alpha$ -nitroso- $\beta$ -naphthol corresponds to the formula,  $(C_{10}H_6O_2N)_3Co \cdot 2H_2O$ , in which cobalt exists in the trivalent state. The precipitate formed according to the directions of Ilinski and v. Knorre, however, is never obtained formula pure because of the presence of the corresponding cobaltous complex. Further, procedures based on the ignition of the precipitate have never been entirely satisfactory. According to Mayr and Feigl,<sup>45</sup> the precipitation of soluble cobaltic salts with  $\alpha$ -nitroso- $\beta$ -naphthol always yields a complex of constant composition. When  $\alpha$ -nitroso- $\beta$ -naphthol is added to a solution of sodium cobaltic nitrite,  $Na_3[Co(NO_2)_6]$ , a purple-red precipitate of pure cobaltic nitrosonaphtholate forms immediately. Since the cobaltic ion concentration in a solution of the complex ion,  $[Co(NO_2)_6]^{-3}$ , is very small, the precipitation may be carried out at extreme dilution. This is the most suitable condition for forming the purest precipitate in an easily filterable form, but it is not satisfactory for the quantitative precipitation of cobalt, since precipitation is never complete. If, however, cobaltous salts are converted to cobaltic hydroxide with hydrogen peroxide in the presence of sodium hydroxide, and the cobaltic hydroxide is then dissolved in acetic acid, a complex trivalent cobalt acetate is formed which permits the quantitative precipitation of cobalt nitrosonaphtholate in a satisfactory manner.

The reagent commonly employed for precipitating cobalt is prepared by dissolving  $\alpha$ -nitroso- $\beta$ -naphthol in ethyl alcohol, acetone or 50 per cent acetic

acid, or by dissolving the sodium salt in water. The use of  $\alpha$ -nitroso- $\beta$ -naphthol in alcohol or acetic acid solution was first suggested by Illinski and v. Knorre,<sup>8</sup> but according to Attack<sup>23</sup> the resulting cobalt compound so formed is somewhat soluble both in alcohol and acetic acid with the result that precipitation is not quite complete. Further, Attack<sup>23</sup> reports that  $\alpha$ -nitroso- $\beta$ -naphthol is gradually precipitated from a 50 per cent acetic acid solution. Attack suggests as a precipitant for cobalt a solution prepared as follows: boil 0.1 g. of  $\alpha$ -nitroso- $\beta$ -naphthol with 20 ml. of water to which has been added 1 ml. of 1 M sodium hydroxide, filter, and dilute the filtrate to 200 ml. Chapin<sup>24</sup> has suggested as a reagent for cobalt a solution of 8 g. of  $\alpha$ -nitroso- $\beta$ -naphthol in 300 ml. of cold glacial acetic acid to which an equal volume of water is added before filtration. Evans<sup>43</sup> has used a solution of  $\alpha$ -nitroso- $\beta$ -naphthol in phosphoric acid for the precipitation of cobalt in the analysis of steel.

Hydrochloric acid is the usual medium in which the precipitation of cobalt is carried out, but this may be replaced with dilute nitric acid without decreasing the accuracy so long as the nitric acid is free of oxides of nitrogen. This is important, since with the use of nitric acid alloys can be brought into solution with iron in the ferric condition without the use of any possible harmful reagents.

Tanii and co-workers<sup>31</sup> have studied the effect of pH upon the precipitation of cobalt, copper, iron, vanadium, palladium and uranium, and report their results in Table 55.

TABLE 55.—SUITABLE pH RANGES FOR PRECIPITATION OF METALS  
WITH  $\alpha$ -NITROSO- $\beta$ -NAPHTHOL

Metal	pH
Cobalt	<8.74
Copper	3.96–13.2
Iron	0.95–2.00
Vanadium	2.05–3.21
Palladium	<11.82
Uranium	4.05–9.38

In addition to cobalt, iron, copper, palladium, vanadium and uranium are also precipitated quantitatively by  $\alpha$ -nitroso- $\beta$ -naphthol.<sup>29</sup> The precipitation of cobalt may be carried out in solutions containing mercury, nickel, chromium, manganese, lead, zinc, aluminum, cadmium, magnesium, calcium, beryllium, antimony and arsenic salts, but silver, tin and bismuth interfere. The latter three elements may be removed as silver chloride, stannic oxide and bismuth oxychloride respectively. No antimony is precipitated from solutions containing a few drops of hydrochloric acid or tartaric acid, and this makes possible the separation of cobalt, iron and copper from antimony. Free phosphoric acid does not disturb the precipitation.<sup>30</sup>

Precipitation with  $\alpha$ -nitroso- $\beta$ -naphthol serves to remove all cobalt from the solution, but early efforts to weigh the precipitate directly led to erroneous results. The final determination has generally been carried out by igniting the

cobalt precipitate to  $\text{Co}_3\text{O}_4$ , or by igniting to the oxide and then reducing to the metal.<sup>32-41,104</sup> The following procedure for determining cobalt in steel is based upon Slawik's<sup>32</sup> modification of the method of Burgass:<sup>42</sup>

**Procedure.** Dissolve 2 g. of the sample to be analyzed in hydrochloric acid and potassium chlorate and expel the excess acid. Add zinc oxide to the solution in a 500-ml. graduated flask and shake vigorously. Dilute to the mark, filter, acidify a 250 ml. aliquot with hydrochloric acid and evaporate to 100 ml. Add 20 ml. of concentrated hydrochloric acid and precipitate cobalt by adding an excess of a 2 per cent alcoholic solution of  $\alpha$ -nitroso- $\beta$ -naphthol. Allow the mixture to stand in a warm place until the supernatant liquid is clear and then filter. Wash the precipitate with concentrated hydrochloric acid and then with hot water, and finally dry, ignite and weigh as  $\text{Co}_3\text{O}_4$ . If much nickel is present, a double precipitation is necessary for a complete separation. If the cobalt content of the steel is low, use a 4 g. sample.

Eder<sup>35</sup> has used a method for determining cobalt in steel which is similar to that of Burgass,<sup>42</sup> in which an acetic acid solution of the reagent is used as the precipitant.

**Procedure.** In a 500-ml. volumetric flask, dissolve 2 g. of steel in 1:10 sulfuric acid, using 20 ml. of the acid for each 1 g. of the sample. Oxidize with nitric acid, being careful to avoid an excess, and then evaporate to a syrupy consistency. Shake frequently toward the end of the evaporation period. Dissolve the residue in about 200 ml. of water and heat to boiling. Add in small portions to the boiling solution a suspension of zinc oxide in sufficient quantity to precipitate all iron. Avoid a large excess of zinc oxide. Cool the mixture, dilute to the mark, and filter through a dry paper. Collect exactly 250 ml. of the filtrate in a 500-ml. beaker, and add 5-8 ml. of hydrochloric acid ( $d = 1.19$ ), and then evaporate to a volume of 100 ml. Dilute to about 150 ml. with water, heat to boiling, and precipitate cobalt with a freshly prepared, hot, 1 per cent solution of  $\alpha$ -nitroso- $\beta$ -naphthol in 50 per cent acetic acid. Use 10 ml. of the reagent for each 0.01 g. of cobalt in the sample. Continue to boil for 5-10 seconds, and allow to stand 1-2 hours with frequent shaking. Filter on an ash-free paper and wash, first with cold 1:5 hydrochloric acid, then with hot 1:5 hydrochloric acid, and finally with hot water. Transfer the filter and precipitate to a weighed crucible, and sprinkle over it a little oxalic acid. Slowly char the paper and finally ignite to  $\text{Co}_3\text{O}_4$ . The factor for cobalt is 0.7443. The quantity of cobalt in the sample is 2 times that found in the aliquot used.

This method gives results which are accurate to within 1 per cent. Congdon and Chen<sup>38</sup> have studied several methods for the determination of cobalt, and report that Eder's method<sup>35</sup> is the most satisfactory.

Germuth<sup>36</sup> has studied the determination of cobalt by means of  $\alpha$ -nitroso- $\beta$ -naphthol in the presence of other ions and claims that the presence of tin in quantities greater than 1.5 per cent interfere with the quantitative determination of cobalt, particularly when small quantities of bismuth are present. This interference appears to be due to the formation of a compound containing tin and

cobalt, possibly a double salt. The results of these studies are shown in Table 56 which is taken directly from the work of Germuth:<sup>36</sup>

In the following procedure, cobalt is separated from nickel by precipitating with  $\alpha$ -nitroso- $\beta$ -naphthol, and it is subsequently determined after igniting to the oxide and reducing to the metal.<sup>3</sup>

**Procedure.** To a neutral solution containing not more than 0.2 g. of nickel and 0.1 g. of cobalt, add 10 ml. of 6 N hydrochloric acid and dilute to 200 ml. Heat the solution to 80° C., and precipitate cobalt by adding an excess of  $\alpha$ -nitroso- $\beta$ -naphthol in 50 per cent acetic acid. Cool, and test for completeness of precipitation by adding a few drops of the reagent. Allow to stand 2-3 hours and filter through a Gooch crucible. Wash with 12 per cent hydrochloric acid until the precipitate is free of nickel and then wash with hot water. Dry, sprinkle a little oxalic acid over the precipitate to prevent too rapid combustion upon heating, and then heat very slowly to redness in an electric oven. Cool, place the crucible in a larger porcelain crucible with a perforated cover and heat in a stream of hydrogen until all cobalt oxide is reduced to the metal. Cool in hydrogen and weigh as metallic cobalt.

Philippot<sup>44</sup> has determined cobalt electrolytically after precipitating with  $\alpha$ -nitroso- $\beta$ -naphthol.

Although cobaltous salts are precipitated completely by  $\alpha$ -nitroso- $\beta$ -naphthol, the precipitate cannot be weighed directly because of its variable composition. This is probably due to the presence in the precipitate of both cobaltic and cobaltous complexes. If, however, the solution is treated with hydrogen peroxide and then made alkaline with sodium hydroxide, cobaltic hydroxide is precipitated; and if this precipitate is dissolved in acetic acid and the resulting solution treated with  $\alpha$ -nitroso- $\beta$ -naphthol, a precipitate is formed which can be dried to constant weight at 130° C., and which corresponds to the formula,  $[\text{C}_{10}\text{H}_6\text{O}_2\text{N}]_3\text{Co}\cdot 2\text{H}_2\text{O}$ . The precipitate contains 9.645 per cent of cobalt. Mayr and Feigl,<sup>45</sup> who have proposed this method, claim that results accurate to within 2 per cent can be obtained.

**Reagent.** Dissolve 4 g. of  $\alpha$ -nitroso- $\beta$ -naphthol by digestion with 100 ml. of cold glacial acetic acid, and to this solution add 100 ml. of hot distilled water. Filter to obtain a clear solution.

**Procedure.** The unknown solution should contain not more than 1-30 mg. of cobalt. Evaporate this solution to a volume of 10-20 ml. and allow to cool, and to the cold solution add 5-10 drops of perhydrol. Then add 2 N sodium hydroxide to precipitate cobaltic hydroxide. Because of the vigorous evolution of oxygen, the reaction should be carried out in a covered beaker. Now add to the reaction mixture 10-20 ml. of glacial acetic acid and dissolve the precipitate by gentle warming. Dilute the mixture to 200 ml. with boiling water, and precipitate cobalt by adding 10-20 ml. of  $\alpha$ -nitroso- $\beta$ -naphthol solution. Heat to boiling, while stirring vigorously, and continue to boil until the precipitate is coagulated. The supernatant liquid should be yellow and perfectly clear. Filter through a porcelain filter crucible and dry at 130° C. Transfer

TABLE 56.—DETERMINATION OF COBALT BY NITROSO- $\beta$ -NAPHTHOL  
PERCENTAGE OF COBALT \*  
(Calculated to  $\text{Co}_2\text{O}_3$ )

Sample No.	Series A 0.02 gm. Co 0.05 gm. Ni	Series B 0.04 gm. Co 0.10 gm. Ni	Series C 0.06 gm. Co 0.20 gm. Ni	Series D 0.08 gm. Co 0.40 gm. Ni	Series E 0.10 gm. Co 0.80 gm. Ni
1	99.987	99.976	99.969	99.965	99.954 <sup>4</sup>
2	99.976	99.972	99.967	99.968	99.953 <sup>8</sup>
3	99.986	99.987	99.970	99.964	99.948 <sup>8</sup>
4	99.975	99.969	99.965	99.991	99.958 <sup>7</sup>
5	99.969	99.975	99.966	99.965 <sup>2</sup>	99.953 <sup>8</sup>
6	99.961	99.988	99.954 <sup>1</sup>	99.963 <sup>8</sup>	99.943 <sup>8</sup>
Avg.	99.976	99.978	99.965	99.969	99.952

\* Volume of solution: 250 ml. Test samples constituting SERIES A contain 0.1 gm. of each of the following cations as chloride:  $\text{Hg}^{+2}$ ,  $\text{Sn}^{+4}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{As}$  (as  $\text{NaHSO}_4$ ),  $\text{Sb}$  (as  $\text{KSnO}_2 \cdot \text{H}_2\text{O}$ ),  $\frac{1}{2} \text{H}_2\text{O}$ ,  $\text{Al}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Bi}$  (as  $\text{BiONO}_3$ ) and  $\text{Pb}$  (as  $\text{Pb(NO}_3)_2$ ). This proportion was increased in increments of 0.1 gm. in each succeeding series of tests. After ignition to  $\text{Co}_2\text{O}_3$ , each precipitate was meticulously examined for the presence of extraneous metals.

<sup>1</sup> Contained  $\text{Cu}^{+2}$  and traces of  $\text{Fe}^{+3}$ .

<sup>2</sup>  $\text{Cu}^{+2}$ ,  $\text{Bi}^{+3}$ , and traces of  $\text{Fe}^{+3}$ .

<sup>3-8</sup> Each of these precipitates contained  $\text{Sn}^{+4}$  ion, and smaller portions of  $\text{Bi}^{+3}$  and  $\text{Ni}^{+2}$  ions.  $\text{Fe}^{+3}$  was present in slight trace. Further experimentation (unpublished) points to the possibility of the existence of a chemical combination of cobalt with bivalent tin.

the remainder of the precipitate to the crucible with 33 per cent acetic acid, and wash the precipitate 3 times with hot acetic acid. Finally, wash 4 times with water heated almost to boiling, and dry at 130° C. to constant weight. The factor for cobalt is 0.0965.

Quantities of cobalt greater than 25 mg. should not be determined in this way, since drying larger quantities of the precipitate requires several hours to attain constant weight. Results obtained using this method are shown in Table 57.

TABLE 57.—DETERMINATION OF COBALT WITH  $\alpha$ -NITROSO- $\beta$ -NAPHTHOL

Cobalt Taken	Weight of Precipitate	Cobalt Found
0.0061	0.0635	0.0062
0.0122	0.1268	0.0122
0.0122	0.1278	0.0124
0.0244	0.2548	0.0245

Hecht and Korkisch<sup>46</sup> have applied the method of Mayr and Feigl<sup>45</sup> to the separation of cobalt from samples containing cobalt, nickel, zinc, and aluminum, and report that the results are not entirely satisfactory.

Several methods have been proposed for the separation of cobalt and nickel<sup>3,5</sup> and cobalt and iron<sup>6,42,43</sup> by precipitating cobalt with  $\alpha$ -nitroso- $\beta$ -naphthol.

Many special analyses of various materials containing cobalt have been effected with the aid of  $\alpha$ -nitroso- $\beta$ -naphthol. For example, cobalt can be determined in steel; <sup>32,35,43,47,48</sup> high speed tool alloys; <sup>47,49</sup> hard alloys of aluminum; <sup>50</sup> nickel-silver; <sup>51</sup> copper; <sup>52</sup> nickel; <sup>53</sup> aluminum; <sup>54,55,57</sup> silicate rocks; <sup>27</sup> manganese ores; <sup>104</sup> in oils, paints and dryers; <sup>59</sup> and in soil.<sup>96</sup>

**Colorimetric determination of cobalt.** The orange to red color which is produced by the reaction of cobalt with  $\alpha$ -nitroso- $\beta$ -naphthol may be used for the colorimetric determination of small amounts of cobalt in paints, varnishes,<sup>68</sup> steel<sup>61</sup> and similar materials.<sup>62</sup> Iron, aluminum and chromium are kept in solution by the addition of ammonium citrate.

Copper, nickel and manganese may interfere, but they can easily be removed prior to the addition of the reagent. In making the color comparisons, the alkalinity of the unknown and the standard solutions should be approximately the same.

**Reagents.**  *$\alpha$ -Nitroso- $\beta$ -naphthol:* Boil 0.1 g. of  $\alpha$ -nitroso- $\beta$ -naphthol with 20 ml. of water and 1 ml. of dilute sodium hydroxide solution, filter, and dilute to 200 ml.

*Ammonium citrate reagent:* Dissolve 500 g. of citric acid in 250 ml. of water and add 500 ml. of ammonium hydroxide (sp. gr. = 0.88).



**Standard cobalt solution:** Dissolve 0.4936 g. of cobalt nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in water, dilute to 1 liter and mix thoroughly. One ml. of this solution contains 0.1 mg. of cobalt.

**Procedure.** Weigh a sample of such size as to contain between 0.05 and 2.0 mg. of cobalt, and heat in a porcelain crucible. Extract the ash with concentrated hydrochloric acid, and if any insoluble matter remains add aqua regia. Finally remove the nitric acid by adding concentrated hydrochloric acid and heating. Evaporate the solution to dryness and dissolve the residue in hot water containing a few drops of 6 N hydrochloric acid, and then dilute to a suitable volume in a volumetric flask. Transfer an aliquot part of the solution to a Nessler tube, and add 5 ml. of the ammonium citrate reagent. Dilute to about 90 ml., and add 5 ml. of the reagent solution, and then dilute with water to 100 ml. Mix well and match the resulting color with that obtained using a standard solution of cobalt which has been prepared in the same manner as the unknown. Comparison may be made by balancing or dilution methods or by duplication.

The above procedure must be modified somewhat if copper, nickel or manganese is present. If copper is present proceed as follows: Make the solution about 0.05 N with hydrochloric acid and precipitate copper by treating with hydrogen sulfide. Filter the precipitate, boil off hydrogen sulfide from the filtrate and complete the analysis as described above.

If nickel is present, proceed as follows:

**Procedure.** Add a few ml. of the ammonium citrate reagent to the neutral or slightly acid solution, dilute to about 100 ml. with water, and heat almost to boiling. Then add a 1 per cent solution of dimethylglyoxime in alcohol and make the mixture slightly alkaline by the dropwise addition of ammonium hydroxide. Stir well and allow to stand for about 5 minutes in a warm place. Filter into a volumetric flask and wash with hot water. Cool, dilute to the mark and mix. Transfer an aliquot part of this solution to a porcelain dish and evaporate to dryness, and then gently ignite the residue. Cool, treat first with aqua regia, then with concentrated hydrochloric acid, and finally evaporate to dryness. Moisten the residue with a drop of 6 N hydrochloric acid, extract with water, and complete the cobalt determination in the usual manner.

Small quantities of manganese apparently do not interfere with the cobalt determination, but when the amount of manganese is considerably greater than that of cobalt, at least a part of it must be removed.

**Reagents.  $\alpha$ -Nitroso- $\beta$ -naphthol:** Add 0.1 g. of  $\alpha$ -nitroso- $\beta$ -naphthol to a solution of 1 ml. of 1 N sodium hydroxide in 20 ml. of water. Heat to boiling for a time, cool, filter, and dilute to 200 ml. This solution keeps indefinitely.

**Ammonium citrate solution:** Dissolve 500 g. of citric acid in 250 ml. of water and add 500 ml. of concentrated ammonium hydroxide.

**Standard cobalt solution:** Dissolve 0.4936 g. of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in sufficient distilled water to make one liter of solution. This solution contains 0.1 mg. of cobalt per ml.

**Procedure.** After evaporating the sample (containing cobalt as the chloride) to dryness on a water bath, dissolve in 25 ml. of 1:10 hydrochloric acid. Dilute if necessary to a definite volume and take a suitable aliquot. Add 25 ml. of 1:1 nitric acid and 0.1 g. of sodium bismuthate. Digest the mixture until the permanganate color disappears and manganese is precipitated. Filter and evaporate the filtrate to dryness on a water bath. Add to the residue 2 ml. of concentrated hydrochloric acid, again evaporate to dryness, and then dissolve the residue in 25 ml. of 1:10 hydrochloric acid.

Transfer the sample to a Nessler tube and add 5 ml. of the ammonium citrate solution. Dilute to 95 ml. with distilled water, and add 5 ml. of the  $\alpha$ -nitroso- $\beta$ -naphthol reagent. Mix well and compare immediately with a standard prepared as follows: mix 25 ml. of 1:10 hydrochloric acid, 10 ml. of ammonium citrate solution and sufficient distilled water to make the total volume 90 ml. Add 5 ml. of the reagent, mix well, and add the standard cobalt solution until the colors match. Adjust the volume to 100 ml. Comparison may be made by balancing or dilution by adding a suitable volume of the cobalt solution before diluting to 100 ml.

Despite the claims of various investigators that the  $\alpha$ -nitroso- $\beta$ -naphthol method for cobalt gives good results, Heinz<sup>63</sup> reports that the reaction is not suitable for a colorimetric determination. The method has been found to possess the disadvantage of a masking of the cobalt color by the necessary excess of the reagent, and by the formation of a precipitate of the cobalt salt. The former weakness cannot be avoided, but the latter is overcome at least in part, by using solvents such as chloroform or carbon disulfide instead of water.<sup>64</sup>

Cobalt can be determined in the presence of manganese, when the latter element is present in quantities ranging as high as 99.40 per cent, by forming the cobalt complex with  $\alpha$ -nitroso- $\beta$ -naphthol and extracting the latter with chloroform and measuring in a photometer, using a green filter.<sup>65</sup> To determine cobalt, a standard curve is first prepared by using a photoelectric photometer with samples ranging from 0.01 to 0.60 mg. of cobalt. This is carried out as follows:

**Reagents.**  *$\alpha$ -Nitroso- $\beta$ -naphthol reagent:* Boil 1.0 g. of  $\alpha$ -nitroso- $\beta$ -naphthol with 200 ml. of water and 10 ml. of 5 N sodium hydroxide. Filter, and dilute to 2 liters.

*Ammonium citrate reagent:* Dissolve 1000 g. of citric acid in 250 ml. of water and 1000 ml. of concentrated ammonium hydroxide.

**Procedure.** Add sufficient 5 N hydrochloric acid to 10 ml. of the ammonium citrate reagent in a 250-ml. flask to make just acid, and then add the solution of the sample. Heat just to boiling, add 25 ml. of the  $\alpha$ -nitroso- $\beta$ -naphthol reagent, and allow the mixture to stand for 2 hours before filtering.

Filter, and wash the paper and precipitate with distilled water to remove as much as possible of the reagent and then dry at 100° C. Extract the precipitate from the filter paper by using 10-15 ml. portions of chloroform until they remain absolutely colorless. Dilute the chloroform extract to exactly 100 ml. with chloroform, and measure the chloroform extract in a photometer, using a green filter. The unknown is determined in the same way.

According to Kahare,<sup>66</sup> cobalt may be separated from manganese without the reagent exercising any effect upon the manganese.

**Titrimetric determination of cobalt.** Bucherer and Meier<sup>67</sup> have attempted to determine cobalt titrimetrically by titrating with a standard solution of  $\alpha$ -nitroso- $\beta$ -naphthol. Their results indicate, however, that the determination cannot be successfully carried out by using a filtration method, in which the end-point is determined by adding the reagent to the filtered solution until no further precipitate forms.

Several successful methods have been used, however, for employing  $\alpha$ -nitroso- $\beta$ -naphthol in a titrimetric procedure. From 1-20 mg. of cobalt can be determined with an accuracy of 0.5 per cent or better in an acetate-buffered solution by means of an amperometric titration. The ratio of  $\text{Co}:\text{C}_{10}\text{H}_6\text{O}(\text{NO})$  in the precipitate at the end-point of the reaction is 1:4. The composition of the precipitate is probably  $\text{Co}[\text{C}_{10}\text{H}_6\text{O}(\text{NO})]_2 \cdot 2\text{C}_{10}\text{H}_6\text{OH}(\text{NO})$ .<sup>68</sup> Copper, palladium, uranium, zirconium, chromium, titanium, vanadium, tin, tungsten, and ferric iron also precipitate with the reagent.

Gapchenko<sup>69</sup> has determined cobalt indirectly by precipitating with  $\alpha$ -nitroso- $\beta$ -naphthol, dissolving the precipitate in acetone, and titrating aliquot parts with a standard solution containing trivalent molybdenum. Molybdenum reduces the nitroso group to the amino compound. An excess of the molybdenum solution is used and the excess determined by titration with ferric ammonium sulfate, using methylene blue as an indicator. Nicolaysen<sup>70</sup> has also determined small quantities of cobalt titrimetrically.

Evans<sup>48</sup> has used a solution of  $\alpha$ -nitroso- $\beta$ -naphthol in phosphoric acid for the precipitation of cobalt in the analysis of steel. The final determination of cobalt is carried out by titrating with standard potassium cyanide solution.

**Reagent.** Place  $\alpha$ -nitroso- $\beta$ -naphthol in a beaker and add syrupy phosphoric acid in the proportion of 50 ml. of the acid to 3.5 g. of the reagent, and then heat the mixture on a hot plate while stirring with a thermometer until the temperature reaches 60° C. Allow to cool before using. The reagent should not be used if more than two days old.

**Procedure.** For samples containing small quantities of cobalt, dissolve 5 g. of the steel in 75 ml. of dilute nitric acid (sp. gr. = 1.2). Smaller quantities of the sample should be used for higher cobalt content. Boil for 10 minutes and allow to cool, and then add 0.5 g. of urea. Dilute the sample to 100 ml. and add the reagent, 1-2 ml. at a time and with stirring, and with an interval of a few seconds between each addition, during which the stirring is continued. When

the precipitate begins to darken and the froth breaks up, and a black scum floats on the surface, add an additional 3-4 ml. of the reagent.

Dilute the mixture with an equal volume of 20 per cent acetic acid and stir, and add 3 ml. of the reagent. Allow the cold mixture to stand for 20-25 minutes with occasional stirring and filter. Wash with a cold solution of 5 per cent nitric acid which has been prepared by diluting 20 per cent nitric acid that has been boiled for 15 minutes. Place the paper and residue in a platinum dish and allow to dry. Place in a muffle and burn off the paper at not too high a temperature.

If vanadium, molybdenum or tungsten is present, fuse with a fusion mixture of alkali carbonates, and dissolve in hot water. Filter and wash the precipitate with hot water. Place the filter in a platinum dish and again burn off the paper. In the absence of these metals, this treatment may be omitted.

Fuse the residue with potassium bisulfate, and continue to heat until potassium sulfate begins to crystallize as a scum on top of the melt. Dissolve the melt in water and transfer to a beaker. Add hydrogen sulfide and heat to boiling. Allow to settle, filter, and wash the precipitate with hot water. Boil the filtrate to expel hydrogen sulfide, and add 25 ml. of boiled-out 20 per cent nitric acid. Evaporate to a volume of 100 ml.

Cool and precipitate exactly as described above, but do not use urea. The resulting precipitate should be crimson in color. Allow to settle, filter and wash as before. Transfer the filter and precipitate to a porcelain crucible (not platinum), dry and ignite. The residue should be black.

When the residue is cool, add 10 ml. of concentrated hydrochloric acid, taking care that the sides of the crucible are rinsed down with the acid. Cover with a watch glass and warm on a steam-bath until solution is complete. Remove the cover. Rinse with hot water and evaporate to dryness on a steam-bath. Rinse the sides of the vessel with 15 drops of concentrated nitric acid, and again evaporate to dryness. Dissolve with 2 drops of nitric acid and 10 ml. of hot water, and transfer the solution to a beaker and allow to cool. If the solution is hazy due to the presence of iron, add to the cold liquid a suspension of barium carbonate in water, a few drops at a time, until a trace of undissolved barium carbonate floats in the solution. Avoid an excess of barium carbonate. Filter and wash with cold water.

Dilute the filtrate to 100 ml. in a flask. Swirl, and add 20 ml. of a saturated aqueous solution of borax. Then add 10 ml. of a 4 per cent potassium iodide solution and titrate with a standard potassium cyanide solution (prepared from 16.8 g. of potassium cyanide and 10 g. of sodium hydroxide diluted to 3500 ml. and standardized) until the precipitate has dissolved and the liquid is only slightly hazy. Determine the volume of cyanide solution used ( $V$ ), and then add an excess to make the total volume equal to  $1.3 \times V + 5$ . Then add 10 ml. of a 10 per cent aqueous sodium carbonate solution and draw a rapid stream of air through the mixture for six minutes. Then add a mixture of 10 ml. of 1:1 ammonium hydroxide and 25 ml. of 20 per cent ammonium chloride solution. Filter and wash the precipitate with water. Finally titrate the filtrate with standard silver nitrate (containing 5.792 g. of silver nitrate per liter) to a permanent opalescence. Now continue the titration with the cyanide solution,

added dropwise, with vigorous shaking, until the solution becomes bright. This is the end-point. Read the burets and record the volume of cyanide and silver nitrate solutions used.

Refill the burets and add a volume of standard cyanide solution which is 0.5 ml. less than the previous buret reading. This is again titrated to opalescence with a silver nitrate solution, and again brought back clear with the cyanide solution. The 2 solutions are then run in alternately, dropwise, until the original amount of cyanide used has been added to the solution and the new end-point is reached. The new silver nitrate reading gives the amount of silver required to balance the amount of cyanide used; and the original silver nitrate reading shows the amount required for the excess of cyanide. The difference between the two readings is a measure of the quantity of cobalt combined with the cyanide. This number, when multiplied by 0.803 gives the weight of cobalt present in milligrams.

The results obtained using this method with samples of pure cobalt are shown in Table 58.

TABLE 58.—DETERMINATION OF COBALT BY CYANIDE TITRATION METHOD

Cobalt Used g.	Titration ml.	Cobalt found g.
0.05000	80.00 — 17.70 = 62.30	0.05001
0.02992	49.80 — 12.55 = 37.25	0.02992
0.02500	44.10 — 13.00 = 31.10	0.02498
0.02000	38.00 — 13.00 = 25.00	0.02006
0.01497	28.45 — 9.80 = 18.65	0.01498
0.01000	24.55 — 12.15 = 12.40	0.00995
0.00500	11.85 — 5.75 = 6.10	0.00490
0.00200	10.70 — 8.20 = 2.50	0.00201

The results of a number of analyses of cobalt and steel using Evans' method are given in Table 59.

TABLE 59.—DETERMINATION OF COBALT IN STEEL

Fe Taken g.	Nickel Taken g.	Copper Taken	Cobalt Taken	Cobalt Found g.
5.0	.050	....	....	.00012*
5.0	.050	....	.002	.00205
5.0	.050	....	.005	.00510
5.0	.050	....	.01	.00980
5.0	.050	....	.025	.02513
5.0	.050	....	.05	.04972
5.0	.050	0.01	.01	.00972

\* Present in Fe.

Chromic salts do not appear to be precipitated to any appreciable extent when using the above method but chromic acid is precipitated. Vanadic acid is also precipitated, but it does not interfere with the cyanide titration. The precipitate obtained in the above procedure contains all cobalt, all copper, a part and probably all of the vanadium, molybdenum and tungsten and a little chromium and iron.

**Detection of cobalt.** Cobalt may be detected by means of the purple-red precipitate which forms when cobalt salts are treated with  $\alpha$ -nitroso- $\beta$ -naphthol. Bellucci<sup>18</sup> states that 1 mg. of cobalt can be detected in 1-2 liters of water by this reaction.

Feigl and Stern<sup>10</sup> have studied the use of  $\alpha$ -nitroso- $\beta$ -naphthol in a spot test for cobalt and recommend the following procedure:

**Reagent.** Dissolve 1 g. of  $\alpha$ -nitroso- $\beta$ -naphthol in 50 ml. of glacial acetic acid and dilute with water to 100 ml.

**Procedure.** Place a drop of the neutral or slightly acid solution to be tested on a strip of filter paper and add a drop of the reagent solution. A brown stain appears if cobalt is present.

If the solution to be analyzed is acid, it should be neutralized after placing on the filter paper by holding over a bottle of ammonium hydroxide. Then, after the addition of the reagent solution, the spot should be treated with a drop of 2 N sulfuric acid. By this procedure 0.05 $\gamma$  of cobalt can be detected at a dilution of 1:1,000,000.

According to Vanossi,<sup>21</sup> manganese, iron, chromium, nickel, titanium, uranium, thorium, zirconium, vanadium and molybdenum interfere. Zinc, aluminum, beryllium, indium, thallium, the alkali metals and the rare earths, however, do not interfere.

Ferric salts interfere with the cobalt test by forming a brown compound with  $\alpha$ -nitroso- $\beta$ -naphthol. The ferric compound is soluble in acids, but a separation of iron and cobalt based on the solution of the iron compound in acids, particularly when formed in the pores of the filter paper, is not satisfactory. If iron is present in the test solution, the most satisfactory procedure is to precipitate the iron, along with cobalt, on the filter paper as ferric phosphate and cobalt phosphate, and then to add the reagent. The yellowish-white ferric phosphate does not react with  $\alpha$ -nitroso- $\beta$ -naphthol, while cobalt phosphate reacts instantly to give the familiar reddish-brown spot. About 0.2 $\gamma$  of cobalt at a concentration limit of 1:240,000 can be detected in the presence of 1850 times as much iron.

The following procedure should be used if the test solution is acid:

**Procedure.** Mix a drop of the acid solution to be tested on a spot plate with a drop of a 1 per cent solution of  $\alpha$ -nitroso- $\beta$ -naphthol in acetone, and add a few drops of 10 per cent sodium phosphate. In the presence of cobalt, a brown coloration appears. This should be compared with a blank when testing for small quantities of cobalt. By this procedure, 0.5 $\gamma$  of cobalt at a concentration of 1:100,000 can be detected in the presence of 1000 times as much iron.

Adamovich<sup>22</sup> has suggested the following procedure for the detection of cobalt in alloy steels:

**Procedure.** Dissolve steel shavings in 1:1 hydrochloric acid, or place on the cleaned surface of the sample several drops of a mixture of nitric and sulfuric acids in water. Transfer the solution to a watch glass. Add 1 drop of nitric acid and heat to boiling. Place a drop of the solution on a strip of filter paper, moisten with a 10 per cent solution of sodium pyrophosphate until decolorized, and then add 1 drop of a 1 per cent solution of  $\alpha$ -nitroso- $\beta$ -naphthol in acetone. A red spot forms if cobalt is present. Cobalt can be detected if present to the extent of 0.3 per cent in steel.

A yellow precipitate is formed when  $\alpha$ -nitroso- $\beta$ -naphthol is added to solution of uranyl salts, and consequently it is necessary to make provision for the presence of uranium, particularly when testing for small quantities of cobalt. Uranium, like iron, may be converted into a non-reacting phosphate by treating with ammonium phosphate, and the test can then be carried out as directed above for testing for cobalt in the presence of iron salts. In this way 0.25 $\gamma$  of cobalt at a concentration of 1:200,000 can be detected in the presence of a thousand times as much uranium.

Cupric salts react with  $\alpha$ -nitroso- $\beta$ -naphthol in much the same manner as do cobalt compounds. By means of potassium iodide, however, cupric salts may be converted into cuprous iodide, which does not react with  $\alpha$ -nitroso- $\beta$ -naphthol, and in this way cobalt may be detected even in the presence of large quantities of copper. The free iodine which is formed in the action between cupric salts and potassium iodide is removed by treating with sodium sulfite. The white insoluble cuprous iodide does not interfere with the test:

**Procedure.** Mix on a spot plate 1 drop of the acid solution to be tested, 1 drop of 2 N hydrochloric acid, and a little 10 per cent potassium iodide solution, and add a little solid sodium sulfite. Then add a drop of a 1 per cent solution of  $\alpha$ -nitroso- $\beta$ -naphthol in acetone and a few drops of a saturated sodium acetate solution. A brown color appears if cobalt is present. As little as 0.2 $\gamma$  of cobalt at a concentration of 1:250,000 can be detected in the presence of 2500 times as much copper.

Palladium salts also yield insoluble reddish-brown colored precipitates with  $\alpha$ -nitroso- $\beta$ -naphthol.

The coloration due to nickel and iron is destroyed by sulfuric acid, and manganese, zinc, tartaric acid and citric acid do not interfere. Large quantities of nickel must be removed.

Atack<sup>23</sup> claims that the sensitivity of the  $\alpha$ -nitroso- $\beta$ -naphthol reaction for cobalt is increased if the sodium salt of the reagent is used instead of an alcoholic solution.

**Reagent.** Boil 0.1 g. of  $\alpha$ -nitroso- $\beta$ -naphthol with 20 ml. of water to which has been added 1 ml. of 1 M sodium hydroxide solution. Filter and dilute to 200 ml. This solution is stable for one year.

**Procedure.** Add 1 ml. of ammonium chloride solution and 1 ml. of the above reagent to a little of the solution to be tested. An orange to red color or precipitate, which is unaffected by the addition of dilute sulfuric acid, indicates the presence of cobalt. With this reaction, 0.001 mg. of cobalt in 1 ml. of solution can be detected.

According to Boettger,<sup>25</sup> as little as 0.006γ of cobalt can be detected in a drop of 0.01 ml. with Atack's reagent.<sup>23</sup>

Thompson<sup>26</sup> claims that  $\alpha$ -nitroso- $\beta$ -naphthol may be used to detect 0.001γ of cobalt at a dilution of 1:2,000,000 by means of a coloroscopic method.

Gutzeit<sup>19</sup> reports that 0.05γ of cobalt can be detected by a contact print method using gelatin-coated paper which is impregnated with  $\alpha$ -nitroso- $\beta$ -naphthol.

Hackl<sup>27</sup> has used  $\alpha$ -nitroso- $\beta$ -naphthol for the detection of cobalt in silicate rocks and Evans and Higgs<sup>101</sup> have used this reagent in a spot test for the detection of cobalt in steel. Smith<sup>28</sup> has used this reagent for detecting cobalt in a group of metals which includes manganese, zinc, cobalt, nickel, calcium, strontium, barium and magnesium. The test may be carried out in the presence of phosphates.

**Detection and determination of palladium.** When  $\alpha$ -nitroso- $\beta$ -naphthol is added to a slightly acid solution containing a palladium salt, a voluminous reddish-brown precipitate of  $(C_{10}H_6O(NO))_2Pd$  is formed. This reaction is extremely delicate and makes possible the detection of palladium in solutions containing only 0.001 mg. of the metal per ml. This reaction may also be used for the quantitative determination of palladium. The precipitate may be washed with hot water and ignited quantitatively to metallic palladium.<sup>71-74,77</sup>

Wunder and Thuringer<sup>75</sup> have used the following procedure for the determination of palladium, and for its separation from copper and iron:

**Procedure.** Dilute the solution containing the chlorides of palladium, copper and iron to 150 ml., and add 20 ml. of concentrated hydrochloric acid and 20 ml. of acetic acid. Heat to boiling and add gradually a freshly prepared solution of  $\alpha$ -nitroso- $\beta$ -naphthol in 50 per cent acetic acid until a slight excess is present. The reagent solution is saturated at boiling. On boiling the solution the red precipitate floats on the surface, while the liquid remains yellow. The quantity of palladium present should not exceed 0.05 g. or filtration will be too difficult. Filter hot, wash with a hot 5 per cent solution of hydrochloric acid and finally with hot water. Dry, ash, and ignite carefully, and finally ignite at high temperature. Reduce the palladium sponge in hydrogen, cool in carbon dioxide, and weigh as metallic palladium.

If the palladium solution is precipitated according to the following directions, pure  $(C_{10}H_6ONO)_2Pd$  is obtained.

**Procedure.** To the palladium solution, which should have a volume of about 20 ml., and which should contain about 30 mg. of palladium, add 10 drops of perhydrol and make the mixture alkaline with sodium hydroxide. Add 30 ml. of glacial acetic acid and dilute to 150 ml. with hot water. Heat to boiling and



precipitate with 15 ml. of a 1 per cent solution of  $\alpha$ -nitroso- $\beta$ -naphthol. Filter through a filter crucible and wash, first with 20 per cent acetic acid, and then with boiling water until the filtrate comes through almost colorless. Dry the precipitate at 135° C. to constant weight. The factor for palladium is 0.2367.

This method is said to be very exact.

Krauss and Deneke<sup>76</sup> have used  $\alpha$ -nitroso- $\beta$ -naphthol for the separation of palladium and platinum. The separation is satisfactory, but the procedure is somewhat difficult, owing to the voluminous character of the precipitate.

**Detection and determination of iron.** An aqueous solution of  $\alpha$ -nitroso- $\beta$ -naphthol reacts with ferrous salts to form a green color, and upon standing a flocculent precipitate appears which is soluble in mineral acids. The precipitate forms in the presence of sodium acetate. An acetic acid solution of  $\alpha$ -nitroso- $\beta$ -naphthol yields a green-black precipitate which consists of a mixture of the ferrous and ferric salts. On long standing or by warming with acids this precipitate changes to the ferric salt.<sup>5,78</sup>

The reaction between  $\alpha$ -nitroso- $\beta$ -naphthol and ferrous ions in an alkaline solution and in the presence of ethyl acetate, which acts as a solvent for the green complex, has a sensitivity of 0.02 $\gamma$  of iron per ml. of solution. This is about the same as that of the thiocyanate reaction. By using a microchemical method, as little as 0.003 $\gamma$  of iron can be detected in 1 drop of solution (0.03 ml.).<sup>79</sup>

The precipitation of the ferric salt with  $\alpha$ -nitroso- $\beta$ -naphthol has been used by Jolles<sup>80</sup> as the basis for a method of determining iron in urine.

**Reagent.** Dissolve 1.2 g. of  $\alpha$ -nitroso- $\beta$ -naphthol in 100 ml. of 50 per cent acetic acid by heating to about 90° C. Allow to stand, filter, and use the filtrate.

**Procedure.** Extract the completely white urine ash with water and a little concentrated hydrochloric acid and warm. Filter, wash, and to the combined filtrate and washings add the reagent as long as any precipitate forms. For 500 ml. of urine (about 2-5 mg. of iron) use 5-10 ml. of the reagent. Stir for 5 minutes with a glass rod, then allow to stand for 5 minutes, and transfer to a filter with a mixture of 250 ml. of acetic acid and 150 ml. of distilled water and wash with this acid until the washings have a pale yellow color. The precipitate consists of  $(C_{10}H_8NO_2)_3Fe$ . The factor for iron is 0.0975.

Fontes and Tivolle<sup>81-82</sup> have used  $\alpha$ -nitroso- $\beta$ -naphthol in the presence of phosphoric acid for the determination of iron in biological liquids. A solution of the reagent in syrupy phosphoric acid precipitates copper, cobalt and ferrous iron but does not precipitate ferric iron.

**Phosphomolybdate reagent.** Dissolve 40 g. of ammonium molybdate in 60 ml. of sodium hydroxide solution ( $d = 1.36$ ) and 100 ml. of water. Boil until all ammonia is expelled and add 200 ml. of water, 250 ml. of phosphoric acid, ( $d = 1.38$ ) and 1 g. of copper carbonate. Boil for 15 minutes and dilute to 1 liter.

**Procedure.** Use an aliquot portion of the unknown solution which contains 0.1-1.5 mg. of iron, but which must not contain cobalt, nickel or copper, and to this add 5-10 drops of 5 per cent methyl orange solution. Neutralize with ammonium hydroxide to a yellow color, and add 10 per cent nitric acid until the color changes to red, and then add 1-2 drops in excess. The pH of the resulting solution should be about 5.0. Reduce the iron by adding 0.1-0.2 g. of zinc-free sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , and add 1 ml. of 6 per cent  $\alpha$ -nitroso- $\beta$ -naphthol in glacial acetic acid. Shake well, allow to stand for a few minutes, and repeat the treatment until the precipitate settles. Filter with gentle suction. Transfer the precipitate to the filter with water and then stop suction. Moisten the precipitate, little by little, with 5 ml. of 30 per cent acetic acid to dissolve all phosphoric acid and excess reagent, and then wash with water. Ignite the residue and reduce with hydrogen.

Dissolve the reduced iron in 5 ml. of the phosphomolybdate solution, whereby the molybdenum is reduced. Titrate the molybdenum blue with standard potassium permanganate solution. After decolorizing, warm to make certain that no small traces of iron remain undissolved. This method is successful in the presence of 5000 times as much phosphoric acid.

Svedenius<sup>83</sup> has also used  $\alpha$ -nitroso- $\beta$ -naphthol to determine iron in organic substances. The ash is dissolved in hydrochloric acid, the resulting solution almost neutralized with ammonia, and iron precipitated from the filtrate by four additions at 7-8 hour intervals of  $\alpha$ -nitroso- $\beta$ -naphthol. The precipitate is dried and ignited in a platinum crucible.

Gantois and co-workers<sup>84</sup> have used  $\alpha$ -nitroso- $\beta$ -naphthol for the determination of iron in glass.

**Separation of iron.** In an acetic acid solution, cobalt, iron, vanadium, palladium, uranium, and copper are quantitatively precipitated with  $\alpha$ -nitroso- $\beta$ -naphthol while aluminum, lead, cadmium, calcium, magnesium, nickel, manganese, mercury and zinc remain in solution. This makes possible a number of important separations of these metals. Solutions of ferric ions are quantitatively precipitated from neutral or weakly acid solutions with  $\alpha$ -nitroso- $\beta$ -naphthol, and this makes possible the separation of iron from chromium, manganese, nickel and zinc with which it is frequently associated. Iron is precipitated as follows:

**Procedure.** Iron should be present as the chloride or sulfate. Neutralize any free acid with ammonium hydroxide to the formation of a precipitate, which is redissolved with a few drops of hydrochloric acid. Heat to boiling and add 1.0 g. of  $\alpha$ -nitroso- $\beta$ -naphthol dissolved in 50 per cent acetic acid for each 0.1 g. of iron that is present. Allow to stand for a few hours, filter, and wash with cold water until a drop of the filtrate upon evaporating leaves no solid residue. Dry, heat carefully over a small flame until no more gas is given off, and then elevate the temperature gradually and finally ignite.

The separation of iron from manganese, zinc and nickel is satisfactory. On long standing or more quickly on heating a red precipitate of  $\text{Cr}(\text{C}_{10}\text{H}_6\text{O}(\text{NO}))_3$ .

is formed from an acetic acid solution containing chromium. When iron is precipitated in the presence of chromium, results are higher due to the precipitation of some chromium. The separation may, however, be carried out by acidifying the solution with hydrochloric acid. This does not prevent the precipitation of iron if only a small quantity of the acid is present. Five ml. of hydrochloric acid in 100 ml. of solution is suitable for this purpose.

Schleier<sup>85</sup> and Atkinson and Smith<sup>86</sup> have reported that  $\alpha$ -nitroso- $\beta$ -naphthol is excellent for the separation of iron from beryllium. Atkinson and Smith also report that iron may be precipitated under conditions in which no uranium is precipitated. Further, the reagent does not precipitate cerous salts, lanthanum, praseodymium, neodymium, terbium, erbium, molybdates and tungstates. Zirconium gives an orange-colored precipitate and ceric salts yield a bright scarlet, flocculent precipitate but precipitation is not complete.

Mathers<sup>87</sup> also states that indium is not precipitated under conditions which permit the complete separation of iron.

**Procedure.** Evaporate the solution containing indium sulfate or chloride and a small amount of iron to a volume of 20-25 ml. Neutralize with ammonium hydroxide and add an equal volume of 50 per cent acetic acid. Precipitate iron by adding 3-5 g. of  $\alpha$ -nitroso- $\beta$ -naphthol dissolved in 50 per cent acetic acid. The precipitation may be carried out either in a hot or cold solution, but the mixture should then stand for several hours before filtering, and should be cold when filtered. Wash the residue with 50 per cent acetic acid and then with water. The precipitate is quite voluminous, and so not more than 50 mg. of iron should be present in the indium solution.

About 0.2-0.3 per cent of indium remains with the iron after a second precipitation.

From a solution having a pH of less than 7, a 2 per cent solution of  $\alpha$ -nitroso- $\beta$ -naphthol in 50 per cent acetic acid precipitates ferric iron completely, while gallium is not precipitated under the same conditions. Papish and co-workers<sup>88-89</sup> have used this reaction for the separation of iron from gallium.

**Procedure.** Carefully add ammonium hydroxide to a mixture of ferric and gallium chlorides until a slight permanent precipitate is formed. Redissolve with a drop of hydrochloric acid, and then add 1-2 drops of acid in excess. Add an excess of 50 per cent acetic acid or ammonium acetate. Then add an excess of reagent dissolved in 50 per cent acetic acid and let stand several hours. Filter and wash, first with 50 per cent acetic acid, and then with water. Dry, transfer the paper and contents to a porcelain crucible and ignite to constant weight, using a Meeker burner. Weigh as ferric oxide.

The results obtained using this method are shown in Table 60.

Ilinski and v. Knorre<sup>5,78</sup> have used  $\alpha$ -nitroso- $\beta$ -naphthol for the precipitation of iron in the presence of aluminum. v. Knorre<sup>90</sup> has also used  $\alpha$ -nitroso- $\beta$ -naphthol for the separation of iron and zirconium. In this procedure the precipitation of iron is prevented by the addition of oxalic acid and by the immediate precipitation of zirconium from a boiling solution after strongly acidifying with hydrochloric acid.

TABLE 60.—SEPARATION OF IRON FROM GALLIUM

Weight of $\text{Fe}_2\text{O}_3$ Taken g.	Weight of $\text{Ga}_2\text{O}_3$ Taken g.	Weight of $\text{Fe}_2\text{O}_3$ Found g.
0.0044	0.0515	0.0044
0.0222	0.0257	0.0221
0.0443	0.0515	0.0443

**Detection and determination of copper.** A brown precipitate of  $\text{Cu}(\text{C}_{10}\text{H}_6\text{O}(\text{NO}))_2$  is formed where  $\alpha$ -nitroso- $\beta$ -naphthol is added to solutions containing copper salts. This compound is soluble in acetic acid, although only traces dissolve in cold 50 per cent acetic acid, which is used as a solvent for the reagent. The compound is insoluble in water and in alcohol. This reaction has been used by Martini<sup>91</sup> for the microchemical detection of copper. v. Knorre<sup>92</sup> has also used this reaction for the separation of copper from lead, cadmium, magnesium, manganese, mercury and zinc.

**Procedure.** Evaporate the solution containing the metals as sulfates or chlorides to a small volume and neutralize any free mineral acids which may be present with ammonium hydroxide. Then acidify with a few drops of hydrochloric acid. Heat almost to boiling and add an excess of  $\alpha$ -nitroso- $\beta$ -naphthol dissolved in boiling 50 per cent acetic acid. Use 5 parts of the reagent for 1 part of copper. Allow the mixture to stand for a few hours, filter, and wash with cold water until a drop of the filtrate evaporated on a strip of platinum leaves no solid residue. Dry the copper precipitate, and heat carefully over a small flame until no more gas is evolved. Elevate the temperature gradually and finally ignite in air to copper oxide.

In the presence of silver salts, the copper precipitate contains some silver. The results obtained by v. Knorre<sup>92</sup> are shown in Table 61.

TABLE 61.

Weight of Copper Taken g.	Other Metal Present g.	Weight of Copper Oxide g.	Weight of Copper g.
0.2031	Cadmium .....1.7550	0.2541	0.2029
0.2031	Magnesium .....0.5350	0.2546	0.2033
0.2031	Manganese .....0.6079	0.2530	0.2021
0.2031	Zinc .....1.2076	0.2530	0.2021
0.1323	Mercury .....0.5884	0.1662	0.1327
0.1323	Mercury .....0.5884	0.1664	0.1329

A similar method has been used for the determination of copper in organic tissue.<sup>95</sup>

**Detection and determination of zirconium.** Zirconium salts react with  $\alpha$ -nitroso- $\beta$ -naphthol to form a greenish-yellow, amorphous precipitate of  $(C_{10}H_6O(NO))_2ZrO$ .<sup>93-94</sup> This compound is insoluble in water and can be dried at 100° C. without decomposition. The formation of this compound can be used for the detection and determination of zirconium.

**Detection of molybdenum and vanadium.** When an alcoholic solution of  $\alpha$ -nitroso- $\beta$ -naphthol is added to an alkaline solution of ammonium vanadate, a green color appears, and this is followed by the separation of a brown precipitate. When the reaction is carried out in an acid solution, however, a voluminous reddish precipitate is formed. No precipitation occurs in neutral solutions. Both precipitates are soluble in concentrated mineral acids.

An acid solution of ammonium molybdate reacts with  $\alpha$ -nitroso- $\beta$ -naphthol to form a voluminous red precipitate. This reaction may be used for the detection of vanadate and molybdate.<sup>58</sup>

**Determination of potassium.** Small quantities of potassium may be determined indirectly by a method developed by Delaville and Carlier.<sup>58</sup>

✓ **Procedure.** Precipitate potassium as the cobaltic nitrite by the usual method and filter. Wash, and dissolve the precipitate in 2 ml. of hydrochloric acid. Neutralize with ammonium hydroxide, and precipitate the cobalt with a 4 per cent solution of  $\alpha$ -nitroso- $\beta$ -naphthol. Ignite the precipitate and reduce with hydrogen at 600° C. (see procedure on determination of cobalt). Place the crucible and contents in the phosphomolybdic reagent of Fontes and Thivolle,<sup>18</sup> which is prepared as follows: mix 40 g. of ammonium molybdate, 10 g. of pure sodium hydroxide and 100 ml. of water and boil 15 minutes. Cool, add 150 ml. of phosphoric acid (sp. gr. 1.35) and 0.5 g. of copper carbonate and again boil for 15 minutes. Dilute to 1 liter with distilled water.

The cobalt dissolves as cobaltous ion, and the molybdic acid is reduced to the tetravalent condition. Titrate the blue solution with potassium permanganate until colorless. From the volume of permanganate solution used, the quantity of cobalt in the precipitate can be determined, and from this the amount of potassium present may be calculated.

By this procedure 0.1 mg. of potassium can be determined with an error which does not exceed 3 per cent.

**Detection of nickel.** A solution of  $\alpha$ -nitroso- $\beta$ -naphthol in 50 per cent acetic acid gives a brown precipitate with nickel. This compound is decomposed by hydrochloric and sulfuric acids.<sup>5</sup>

**Detection of boron.** A mixture of borax and  $\alpha$ -nitroso- $\beta$ -naphthol turns bright green when moistened with cold water. An excess of boric acid prevents this reaction.<sup>100</sup>

**Determination of phosphate.** Nadler<sup>102</sup> reports that  $\alpha$ -nitroso- $\beta$ -naphthol may be used in place of 1,2,4-aminonaphtholsulfonic acid in the Fiske-Subbarow<sup>108</sup> method for the determination of phosphates. The reagent is dissolved

in a sulfite-bisulfite mixture, and is both sulfonated and reduced to the amino-sulfonic acid.

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### $\beta$ -NITROSO- $\alpha$ -NAPHTHOL

$C_{10}H_7O_2N$

Mol. Wt. 173.16

Beil. Ref. VII, 715.

$C_{10}H_6(NO)OH$

**Use:** Detection of cobalt, copper, and zirconium.  
Determination of zirconium.

$\beta$ -Nitroso- $\alpha$ -naphthol is a yellow or greenish-yellow crystalline solid which melts at 147-148° C. It is soluble in hot water, very soluble in alcohol, but only slightly soluble in ether.

**Preparation:** Dissolve 100 g. of  $\alpha$ -naphthol and 100 g. of anhydrous zinc chloride in 600 ml. of ethyl alcohol. Heat to boiling and add slowly an aqueous solution containing 50 g. of sodium nitrite. Boil the mixture vigorously for 2 or 3 hours under reflux, and allow to cool. Filter off the red zinc salt, and wash with a little cold alcohol. Suspend the solid in water and acidify with hydrochloric acid. Filter the free nitroso compound with suction and thoroughly wash with cold water. Then digest with a solution of 30 g. of potassium hydroxide and 300 ml. of alcohol. Again filter, wash the precipitate with alcohol, dissolve in hot water, and precipitate the free  $\beta$ -nitroso- $\alpha$ -naphthol by the addition of hydrochloric acid.

Dissolve the impure material in boiling alcohol, filter, and add successive small portions of water to the filtrate. When the filtrate is cool, filter, and dry the crystals.<sup>1</sup>

**Detection and determination of cobalt.**  $\beta$ -Nitroso- $\alpha$ -naphthol, like  $\alpha$ -nitroso- $\beta$ -naphthol, yields a reddish-brown, slightly soluble precipitate with solutions of cobalt salts.<sup>2</sup> This compound is an inner-complex salt, similar in type to that formed with  $\alpha$ -nitroso- $\beta$ -naphthol.

Bellucci<sup>3</sup> has studied this reaction and reports that 1 mg. of cobalt in 17 liters of solution can be detected by means of  $\beta$ -nitroso- $\alpha$ -naphthol, while the reaction with the  $\alpha,\beta$ -isomer can be used to detect only 1 mg. in 2 liters.

Jung and co-workers<sup>4</sup> suggest the following method for the detection of cobalt:



**Procedure.** To 1 ml. of a neutral cobalt solution, add 3 drops of a 0.1 per cent alcoholic solution of  $\beta$ -nitroso- $\alpha$ -naphthol and 2 drops of a 1 M solution of sodium hydroxide and Rochelle salt. If only very small quantities of cobalt are present, allow to stand 30 minutes, and then add 0.5-1.0 ml. of benzene and 2-5 drops of 5 N sulfuric acid. Shake vigorously for a few minutes and dissolve the cobalt complex and excess reagent in benzene. The benzene layer is colored red with as little as 3-4 $\gamma$  of cobalt.

To eliminate the excess reagent, again make the aqueous phase basic to dissolve the excess reagent and form a yellow solution. The benzene layer remains red.

If heavy metals are present, pour off the benzene layer and add a dilute solution of sodium hydroxide and shake to extract the excess reagent. With small quantities of other metals, make a blank test and compare.

Jung<sup>4</sup> claims that with this procedure as little as 0.03 $\gamma$  of cobalt per ml. can be detected. The concentration limit is 1:34,000,000.

Yoe and Barton<sup>5</sup> have studied the use of  $\beta$ -nitroso- $\alpha$ -naphthol for the colorimetric determination of cobalt, and report that while the method is very sensitive, the great influence of the concentration of ammonia upon the development of the color, and the low solubility of the cobalt nitrosonaphtholate present serious problems in its use.

The optimum conditions for the determination are given as follows:

**Reagent.** Mix 0.1 g. of  $\beta$ -nitroso- $\alpha$ -naphthol with 20 ml. of water and add 1 ml. of 1 N sodium hydroxide, and then warm the mixture until the reagent is completely dissolved. Dilute to 200 ml. The resulting solution contains 0.05 per cent of the reagent. This solution is stable for several weeks.

**Procedure.** Mix 10 ml. of a solution containing 10 p.p.m. of cobalt with 5 ml. of 60 per cent ammonium citrate solution and 5 ml. of 3 N ammonium hydroxide solution. Dilute to 85-90 ml. and add 3 ml. of the 0.05 per cent solution of the reagent. Dilute to exactly 100 ml. and mix thoroughly. Cobalt is determined in this solution by determining the light transmission in a spectrophotometer. The wave length of 550  $m\mu$  is the most suitable for the color measurement. This method may be used to detect as little as 0.005 p.p.m. of cobalt.

If the ammonium hydroxide and cobalt solutions are mixed before the addition of ammonium citrate, the absorption is much less; hence, the order of mixing of the reagents is very important in making an accurate determination.

Nickel interferes with this determination, and makes the difference in the absorption somewhat less, probably by reacting with the reagent. Determinations may be made, however, without an exact knowledge of the concentration of nickel. Interference due to copper is somewhat greater than with nickel. Ferric iron may be present, but not to exceed a concentration of 10,000 times that of cobalt.

The principal advantages of this method are its high sensitivity and reproducibility, while the chief disadvantages are the greater influence of concentration of ammonia and low solubility of the cobalt compound.

Cardini, Jung and Fuksman<sup>6</sup> have used essentially the same method described above for the detection of cobalt, and for the colorimetric determination of small quantities of cobalt. Add the  $\beta$ -nitroso- $\alpha$ -naphthol to a slightly basic solution of the cobalt solution, and treat the precipitate which forms with sulfuric acid and benzene. The colored complex passes into the benzene layer. Then add Rochelle salt and sodium hydroxide to the mixture to remove the excess reagent from the benzene solution. By comparing the color of the benzene layer with that formed from cobalt solutions of known concentration, from 1-16 $\gamma$  of cobalt can be determined satisfactorily.

**Detection of zirconium.** An alcoholic solution of  $\beta$ -nitroso- $\alpha$ -naphthol yields an insoluble, deep red complex salt with an aqueous solution of a zirconium salt. The precipitate corresponds in composition to  $(C_{10}H_6O_2N)_2ZrO$ . When an alcoholic solution of  $\beta$ -nitroso- $\alpha$ -naphthol is added to a hydrochloric acid solution of zirconium, a deep red color forms, but no precipitation occurs. Upon the addition of sodium acetate, however, a precipitate is formed.<sup>7-8</sup>

The following procedure may be used for the detection of zirconium:

**Procedure.** Impregnate filter paper with a 2 per cent alcoholic solution of  $\beta$ -nitroso- $\alpha$ -naphthol and allow to dry. Acidify the solution to be tested with hydrochloric acid, and place a drop of this solution on the prepared filter paper. A red to yellow-brown spot appears depending upon the concentration of zirconium. This spot becomes more vivid upon the addition of a little dilute acid.<sup>9</sup> By means of this reaction 0.2 $\gamma$  of zirconium can be detected at a concentration of 1:250,000.

In the presence of large amounts of sulfate or fluoride, the sensitivity of the reaction is diminished somewhat, although interference due to sulfate can be eliminated by a preliminary precipitation with barium chloride. A very sensitive test for zirconium may be carried out by developing the color in a large volume of solution and observing in a Nessler tube or similar vessel.

Quantities of free sulfuric acid must be absent in making the test, since this inhibits the color, but the color is more intense in the presence of approximately 3 N hydrochloric acid.

**Procedure.** If the solution is strongly acid, precipitate zirconium with ammonium hydroxide, filter, and wash well with water, and then dissolve in warm 1:3 hydrochloric acid. Add to this solution an equal volume of a 1 per cent alcoholic solution of  $\beta$ -nitroso- $\alpha$ -naphthol and observe the color in a Nessler tube. The limit of sensitivity of this test is 0.001 g. of  $ZrO_2$  per ml.

An aqueous solution of titanium chloride, which is acid due to hydrolysis, gives no color with an alcoholic solution of  $\beta$ -nitroso- $\alpha$ -naphthol; but when a solution containing the titanium salt is neutralized with sodium acetate, the addition of an aqueous potassium salt of the reagent produces an orange-red amorphous precipitate of a complex salt of titanium and the reagent. This compound, however, dissolves with a complete disappearance of the color when acidified with hydrochloric acid. Therefore in an acid medium the zirconium reaction is not influenced by the presence of titanium salts, and offers a con-

venient means of detecting zirconium in the presence of titanium. The following procedure is used:

**Procedure.** Precipitate zirconium and titanium together with ammonium hydroxide at ordinary temperatures, filter, and wash the precipitate well with water. Dissolve the precipitate in warm 1:3 hydrochloric acid and add an equal volume of a 1 per cent alcoholic solution of the reagent.

Aluminum, thorium, cerium, and lanthanum salts do not interfere, but iron must be removed.

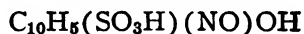
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## 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

$C_{10}H_7O_5NS$

Mol. Wt. 253.22

Beil. Ref. XI, 331.



**Use:** Detection of cobalt, copper and iron.

2-Nitroso-1-naphthol-4-sulfonic acid is a brownish-yellow crystalline solid, forming with  $3\frac{1}{2}$  molecules of water. The compound becomes anhydrous at  $115^\circ C$ . The anhydrous compound is red in color. It is very soluble in water and alcohol, and is very stable.

**Preparation:** Dissolve 24.6 g. of the sodium salt of 1-naphthol-4-sulfonic acid in 300 ml. of water and add 19 ml. of concentrated hydrochloric acid. Add dropwise with cooling a concentrated solution containing 6.9 g. of sodium nitrite. Allow to stand until the crystalline precipitate has formed and then filter with suction. Dissolve the precipitate in 500 ml. of water and add 50 ml. of hydrochloric acid. Separate the crystalline product which forms.<sup>1</sup>

**Detection of cobalt, copper and iron.** 2-Nitroso-1-naphthol-4-sulfonic acid is a strong acid which is capable of reacting to form two series of salts. Only the hydroxyl group, however, is involved in the most characteristic color reactions of the reagent. The colored products correspond in composition to those of  $\beta$ -nitroso- $\alpha$ -naphthol.

Hoffmann<sup>2</sup> first observed the color reaction with cobalt and the reagent, and this has more recently been studied by Sarver<sup>3-4</sup> as a means of detecting cobalt,

iron and copper. A 1 per cent aqueous solution of the nitroso compound is used as the reagent. This gives a red color with cobalt, an orange color with copper, and a green color with ferrous salts. Precipitates are formed with concentrated solutions of these metals. The color reaction with iron is more intense at pH 5, while the most suitable range for cobalt is 7.8. If the solution is not too dilute, however, a good color may be obtained at any pH above 3. Ferric iron causes interference by reducing the intensity of the color, but this interference may be eliminated by the addition of a soluble fluoride. Chromium does not interfere, and other common ions except cyanides exert no harmful influence. Cyanides prevent the reaction.

The proper pH for the test may be obtained with the use of sodium acetate and acetic acid.

When present in pure solutions, either cobalt or iron can be detected at a dilution of 1:20,000,000. The copper reaction is somewhat less sensitive. About 0.01% of any of the ions can be detected by means of a spot test.

There is no satisfactory method for suppressing the mutual interference of copper, cobalt and iron. Iron may be eliminated by oxidizing to the ferric state and adding fluoride, and cobalt may be removed according to the usual procedures. Nickel interferes only when present in high concentrations.

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## ***o*-NITROSOPHENOL**

Synonym: Benzoquinone-1,2-monoxime, *o*-quinonemonoxime

$C_6H_5O_2N$

Mol. Wt. 123.11

Beil. Ref. VII, 600.



**Use:** Detection of cobalt, copper, iron, mercury, nickel, palladium and zinc. Determination of cobalt and iron.

*o*-Nitrosophenol is an oily liquid. The sodium salt consists of red-green shimmering leaves which explode on heating. The compound is easily soluble in water with the formation of a dark, reddish-brown solution. It is only slightly soluble in ether and benzene.

**Preparation of reagent and reactions with metals:** *o*-Nitrosophenol and some of its metallic salts were first prepared and described by Baudisch and co-workers.<sup>1-2</sup> These metal salts are typical organic inner-complex compounds and are therefore usually highly colored. Baudisch mentioned as early as 1912 that the formation of the red-violet, water-soluble copper complex constitutes one of the most sensitive qualitative reactions for cupric salts. Owing to the difficulty of preparing the reagent, however, this reaction has been of comparatively little use until recently when Baudisch<sup>3-4</sup> discovered new and very simple methods for preparing the reagent.

*o*-Nitrosophenol forms in weakly acid solutions strongly colored complex salts with several of the heavy metals. The grayish-brown cobalt compound, the green palladium compound and the brown ferric compound are distinguished from other metallic complexes in that they are easily soluble in petroleum ether, and can thus be extracted from the aqueous solution in which they are formed. The other group of metallic complexes consists mainly of those formed from divalent copper, mercury, nickel, zinc and divalent iron. All these metal salts are soluble in water or certain organic solvents, such as ether, depending upon the conditions under which they were formed; but all are insoluble in petroleum ether. The copper and mercury complexes are reddish-violet, the nickel and zinc compounds are red, and the ferrous compound is green.

The colors of all the above complexes are stable for at least several hours and are so intense that most of the ions can easily be detected in concentrations of 1 part in 10,000,000. In 1915 Baudisch and Rothschild<sup>1</sup> proposed the following method for the preparation of the reagent and the detection of copper.

**Procedure.** Mix 5 g. of *o*-nitroanisol and 8 g. of amyl nitrite in a flask with 50 ml. of concentrated ammonia and 20 ml. of 96 per cent alcohol. Shake well and to this add with shaking 7.5 g. of zinc in small portions. Warm finally to the temperature at which the alcohol boils. The reduction is ended in about one-half hour. Filter with suction and extract the filtrate twice with ether to remove the unchanged *o*-nitroanisol. Mix the aqueous layer with an excess of copper acetate and acidify with acetic acid. The precipitate is purified from benzene and consists of the copper salt of *o*-methoxynitrosophenylhydroxylamine. Wash the precipitate with water and boil with xylene and decompose with lime, and finally extract with petroleum ether and acidify.

The color of the petroleum ether solution is green, but if this is shaken with a solution containing a copper salt, after the addition of ether, the latter becomes red.

More recently Baudisch<sup>3</sup> has proposed the following method for preparing *o*-nitrosophenol:

**Procedure.** Suspend 0.5 g. of freshly prepared cuprous hydroxide in 200 ml. of distilled water in which is dissolved 0.5 g. of potassium nitrite. The pH of the solution should be 9.9. Add purest benzene and stir, and then add dilute hydrochloric acid until the pH is 2.5. Then add 1 ml. of 30 per cent hydrogen peroxide. Stir and the deep red copper salt of *o*-nitrosophenol is formed. Acidify with hydrochloric acid and extract with petroleum ether.

**Determination of cobalt.** Cronheim<sup>5</sup> has based a method for the colorimetric determination of cobalt upon the color which the latter forms when treated with *o*-nitrosophenol. In this procedure the aqueous solution of the cobalt salt is shaken with a solution of *o*-nitrosophenol in petroleum ether; and, after the two liquids have separated, the color intensity of the petroleum ether solution is measured in a colorimeter.

There are very few limitations to the use of this method. Most important among these is the fact that acids whose cobalt salts are insoluble at pH 4.0,

such as the phosphate and oxalate, must be absent. The proper control of the pH of the solution is very important. The strongest color intensity for a given cobalt concentration is obtained at a pH of 3.8 to 4.4. Therefore, a pH of approximately 4.0 must be maintained by the use of a suitable buffer solution, which at the same time should form a complex compound with ferric iron without affecting the state of the cobalt ions. A mixture prepared by dissolving 2.1 g. of citric acid in 88.5 ml. of water and adding 11.5 ml. of 1 N sodium hydroxide is suitable for this purpose. A buffer consisting of tartaric acid and sodium hydroxide may also be used. An acetate buffer cannot be used, since its iron complex is not sufficiently strong to prevent the reaction of the iron with *o*-nitrosophenol. The following procedure may be used:

**Reagent.** The method used for preparing the reagent is that described by Baudisch<sup>8</sup> (above). Since the reagent can be prepared and is stable only in solution, the concentration cannot be expressed in the usual manner, but must be controlled by the following tests which are made at regular intervals:

(a) Shake 1 ml. of the *o*-nitrosophenol solution with 5 ml. of a 1 per cent copper sulfate solution in a test tube. The petroleum ether layer should be absolutely colorless.

(b) Shake 2 ml. of the *o*-nitrosophenol solution with 5 ml. of a solution prepared by dissolving 10 mg. of copper sulfate pentahydrate in 1 liter of distilled water. The aqueous solution should be violet in color, while the petroleum ether layer should remain yellowish-green.

The solution of *o*-nitrosophenol in petroleum ether is stable for 2-3 weeks if kept in a refrigerator:

**Procedure.** Neutralize the solution of the cobalt salt, if necessary, by using a spot test with methyl orange. Dilute the solution so that it contains not more than 1.5 mg. of cobalt in 100 ml. Pour 10 ml. of this solution into a small separatory funnel, add 5 ml. of the citrate buffer, and 2 ml. of the reagent in petroleum ether, and then shake the mixture vigorously for 15-20 seconds. Allow to stand for a short time and separate the brown petroleum ether layer from the water solution and transfer to a glass stoppered flask graduated at 12 ml. Repeat this procedure 2 times, using each time 2 ml. of the *o*-nitrosophenol solution. Then wash the aqueous solution twice with 2 ml. portions of pure petroleum ether. Add the washings to the brown cobalt extract, and then dilute the entire mixture to 12 ml. with petroleum ether. Place this solution in the 10 ml. cell of a colorimeter and make the determination in the usual manner.

Ferric salts interfere with the cobalt reaction, but this interference can be eliminated in three ways: (a) by precipitation of the iron in an acid solution with cupferron; (b) by reduction of the ferric iron to the ferrous state with isoascorbic acid; or (c) by the formation of complex ions with the ferric ion.

**Determination of iron.** Cronheim and Wink<sup>6</sup> used the color reaction of *o*-nitrosophenol with ferrous iron for the colorimetric determination of iron. Iron alone of the metals which form colored complexes with *o*-nitrosophenol,

forms a green, water-soluble complex. In this procedure a solution of *o*-nitrosophenol in petroleum ether is shaken with an aqueous solution of the ferrous salt, whereupon the complex green iron salt is formed immediately and quantitatively. The use of the water-immiscible solvent for the reagent has a very important advantage in this procedure: since free *o*-nitrosophenol in an organic solvent is yellowish-green in color it is possible to observe directly whether or not an excess of the reagent is present. An excess should be used in all determinations. If the petroleum ether solution of *o*-nitrosophenol becomes colorless after shaking with the ferrous salt solution, an insufficient quantity of the reagent has been added. The aqueous solution of the ferrous salt when shaken with *o*-nitrosophenol solution in petroleum ether becomes deep green, and after the two liquids have been separated the green aqueous solution is measured in a colorimeter in the usual manner. The green ferrous complex is stable for at least 24 hours in the absence of very strong oxidizing agents or of light.

As in the determination of cobalt, the proper control of the hydrogen ion concentration is of the greatest importance. In the formation of water-soluble compounds, a low pH prevents the quantitative formation of the complex. On the other hand, if the pH is too high a mixture of two compounds is formed whose general formula can be written as N-Me-R and N-Me-N, in which N represents the *o*-nitrosophenol group. These two compounds differ somewhat in their color and solubility. For the determination of ferrous iron, the most suitable pH range is 5.1-5.3.

**Reagent.** The reagent is prepared and tested by the method described for the determination of cobalt, page 326.

**Procedure.** Neutralize the ferrous salt solution and dilute so that it contains not more than 1γ of ferrous iron per ml. of solution. Place exactly 5 ml. of this solution in a separatory funnel and mix with exactly 5 ml. of an acetate buffer solution of pH 5.2. Add 5 ml. of *o*-nitrosophenol reagent and shake the mixture vigorously for 15-20 seconds, and then allow the two liquids to separate in the funnel. Remove the petroleum ether as completely as possible by means of a pipet, and shake the green aqueous solution with a second 5-ml. portion of *o*-nitrosophenol solution. Again allow the liquids to separate. The petroleum ether should still be yellowish-green due to the presence of an excess of *o*-nitrosophenol. Filter the green aqueous solution through a filter paper directly from the separatory funnel into a 30 mm. cell of a colorimeter. The filtration aids in clearing the water solution completely of the last drops of petroleum ether, and prevents the formation of bubbles which might cling to the cell walls and so interfere with an accurate determination.

Results indicate that this method is one of the most sensitive for the quantitative determination of ferrous ions. The method appears to be at least three times as sensitive as the 2,2'-dipyridyl method. The limitations of the new method are few. The most important is the necessity of having ferrous iron present in the ionic state. This means that complex-forming substances, such as phosphoric and oxalic acids must be absent. Ferric iron, cobalt and palladium do not interfere because their *o*-nitrosophenol salts are soluble in petro-

leum ether and are therefore extracted during the reaction and in the separation of the petroleum ether layer. If ferric iron is present, strong light must be excluded since under its influence ferric iron is reduced to a certain extent by *o*-nitrosophenol and therefore causes high results. The other heavy metals which form water-soluble colored complexes, such as copper, nickel, mercury and zinc may interfere. In their presence, however, the *o*-nitrosophenol complexes of these and other less important metals are all red or reddish-violet in color, and in their presence ferrous iron can be determined by the use of suitable color filters.

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#### 4-NITROSORESORCINOL

$C_6H_5O_3N$

Mol. Wt. 139.11

Beil. Ref. VIII, 235.

$C_6H_3(OH)_2NO$

**Use:** Detection of cobalt and palladium.

4-Nitrosoresorcinol is a light yellow crystalline solid. It is very unstable.

**Preparation:** Mix a solution of 33 g. of resorcinol in 90 ml. of absolute alcohol with a solution of 24 g. of potassium hydroxide in a little absolute alcohol, and treat in a freezing mixture with 39 g. of isoamyl nitrite. Cool for 3 or 4 hours in ice, and wash the separated potassium salt with alcohol and ether. Shake 50 g. of the salt with water to form a thin paste and then acidify with careful cooling with 100 g. of 25 per cent sulfuric acid in which pieces of ice are floating. Filter off the light yellow crystalline solid which forms and recrystallize from dilute alcohol.<sup>1</sup>

**Detection and determination of cobalt.** 4-Nitrosoresorcinol reacts with cobaltic nitrate to form a red complex having the formula  $(C_6H_4O_3N)_3Co$ . This is soluble in alcohol, but is only slightly soluble in ether and is insoluble in chloroform.

This reaction can be used for the detection and colorimetric determination of small quantities of cobalt.<sup>2</sup> 4-Nitrosoresorcinol possesses the advantage over other reagents which have been used for this purpose, for, although less sensitive than some other reagents such as  $\beta$ -nitroso- $\alpha$ -naphthol, solutions of the cobalt complex of 4-nitrosoresorcinol are stable for several weeks.

The color of the reagent varies markedly with the pH of the solution: below pH 2.5 the color is pale greenish-yellow, and this increases in intensity and finally becomes orange at about pH 5.6. An increase in the pH above 7.0 results in a slow decrease in intensity of color. The pH also influences the red color of the cobalt complex. No visible reaction occurs at all at pH lower than 2.0.



The intensity of the color increases from pH 2.0 to 5.6, and is practically constant from 5.6 to 6.3, and then decreases slightly as the pH is increased above 6.5. A pH of 6.0 seems to be the most suitable for the determination.

The following procedure may be used for the determination of cobalt in the absence of interfering substances.

**Reagent.** *4-Nitrosoresorcinol solution:* Dissolve 0.05 g. of the sodium salt of 4-nitrosoresorcinol in 100 ml. of distilled water. This solution is stable for several weeks.

**Buffer solution:** A buffer solution having pH of 6.0 is prepared by adding 363 ml. of 0.5 M sodium hydroxide solution to 500 ml. of 0.4 M potassium acid phthalate and diluting with water to 1 liter. The pH of the buffer is practically unchanged when diluted from 25 to 100 ml.

**Procedure.** Transfer the solution containing cobalt, or a suitable aliquot, to a 100-ml. volumetric flask and add 25 ml. of the buffer solution, and 5 ml. of the reagent, and then dilute to the mark with water. Mix thoroughly and compare the resulting color with that produced in standards containing known quantities of cobalt.

Using Nessler tubes, 1 part of cobalt in 20,000,000 parts of solution may be determined at cobalt concentrations ranging from 0.0 to 0.08 mg. per 100 ml.; 1 part in 10,000,000 at a concentration of 0.08 to 0.2 mg. per 100 ml.; and 1 part in 5,000,000 at a concentration of 0.2 to 0.25 mg. per 100 ml. The determination can be made somewhat more sensitive by using a spectrophotometer. In this way 1 part of cobalt in 50,000,000 parts of solution may be detected.

Cupric ions react with 4-nitrosoresorcinol to form a complex that is nearly as intense in color as that formed with cobalt. In the determination of cobalt, the quantity of copper present must not exceed 0.01-0.02 mg. Palladium ions react with 4-nitrosoresorcinol to form a colored palladous complex which at low concentrations is almost as intense as that with cobalt; hence, palladium must be absent in the determination of cobalt. 4-Nitrosoresorcinol also reacts with ferric ions to yield a green solution at concentrations as low as 0.1 p.p.m. The use of citrate or tartrate does not completely eliminate this interference. 4-Nitrosoresorcinol is not recommended for the determination of cobalt if iron is present. Zinc and cadmium are without effect upon the determination if present in concentrations lower than 1,000 p.p.m. Barium, calcium, magnesium and lead do not interfere at concentrations below 100 p.p.m.; manganese, thorium, yttrium, and ytterbium do not interfere in less than 10 p.p.m.; chromium at less than 5 p.p.m.; silver, aluminum and mercury at less than 1 p.p.m. and titanium and zirconium at less than 0.5 p.p.m.

Nickel forms a colored complex with 4-nitrosoresorcinol under the conditions used for the determination of cobalt, and interferes if present in concentrations greater than 0.5 p.p.m. By means of the following procedure, however, interference due to nickel may be eliminated:

**Procedure.** Transfer the solution to be tested to a 100-ml. Erlenmeyer flask, add 25 ml. of the buffer described above and 5 ml. of the reagent. Heat

on a water-bath for a time and cool, and transfer quantitatively to a 100 ml. volumetric flask and dilute to the mark with water.

The period of heating on the water-bath is determined by the quantity of cobalt and nickel present. The heating time may be determined by reference to Table 62.

TABLE 62.

Time	Quantity of Nickel	Final Concentration of Cobalt
2 hours	5 mg.	1 p.p.m.
3 hours	5 mg.	1.5 p.p.m.
4 hours	10 mg.	1 p.p.m.
6 hours	10 mg.	1.5 p.p.m.
6 hours	15 mg.	1 p.p.m.
10 hours	15 mg.	1.5 p.p.m.

A longer heating period is required if the volume is greater than 40 ml. during the heating period. Compare as described as above.

**Detection and determination of palladium.** Palladium nitrate reacts with 4-nitrosoresorcinol to form a highly colored complex, corresponding in composition to  $(C_6H_4O_3N)_2Pd$ . This reaction may be used for the detection and colorimetric determination of palladium.<sup>3-4</sup>

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### 1-NITROSO-2-HYDROXY-3,6-NAPHTHALENEDISULFONIC ACID (SODIUM SALT)

Synonym: Nitroso-R-salt



Mol. Wt. 377.26



**Use:** Detection of barium, calcium, cobalt, iron, lead, nickel and silver. Determination of cobalt, iron and potassium.

Nitroso-R-salt is a golden yellow crystalline solid. It is soluble in about 40 parts of water, and is only slightly soluble in methyl alcohol and ethyl alcohol.

**Preparation:** *R-salt:* Warm 1 part of  $\beta$ -naphthol with 3 parts of concentrated or fuming sulfuric acid for 12 hours at 100-110° C., or with 4 parts of concentrated sulfuric acid for 5-6 hours at 125-150° C. Dilute the reaction mixture with water and add barium carbonate to the boiling solution. Filter off the barium salt of the monosulfonate, and evaporate the filtrate. Allow the mixture to stand until the jelly-like mass of the disulfonic acid has crystallized, and then extract from the mixture with cold water the G-acid (2-naphthol-6-8-disul-

fonic acid). The R-acid remains insoluble. The separation of these compounds may be effected by converting the mixture of R- and G-acids to the sodium salts, and heating with 3-4 times their quantity of 80-90 volume per cent ethyl alcohol, whereby the G-salt dissolves and the R-salt remains insoluble.

**Nitroso-R-salt solution:** Dissolve 35 g. of pure R-salt in 400 ml. of water and acidify the solution with 10 ml. of concentrated hydrochloric acid. Cool to 8-10° C. and stir while a cold solution of 7.2 g. of sodium nitrite in 20 ml. of water is added dropwise over a period of 30 minutes. Stir for some time after all of the nitrite has been added and then filter with suction on a Buchner funnel. Add sufficient cold water to the residue to form a thin paste and again filter with suction. Wash with cold water and finally with ethyl alcohol.<sup>1</sup>

**Detection of cobalt.** Nitroso-R-salt reacts with solutions of cobaltous salts to form a beautiful red compound, which is very stable and is analagous to the cobalt complex of  $\alpha$ -nitroso- $\beta$ -naphthol.

This reaction was first observed by Van Klooster<sup>1</sup> and has since been used by various investigators for the detection of cobalt.<sup>2-4</sup>

**Reagent.** Dissolve 0.5 g. of nitroso-R-salt in 100 ml. of water.

**Procedure.** To 2 ml. of a solution to be tested add 1 g. of powdered sodium acetate and 2 ml. of the reagent solution. Heat to boiling over a small flame, and add gradually 1 ml. of concentrated nitric acid, and then continue to boil for about 1 minute. The appearance of a permanent red color indicates the presence of cobalt. By means of this reaction as little as 0.03 mg. of cobalt per ml. can be detected.

Ferrous salts react with the reagent to yield a green colored compound, while nickel salts form a brownish-red color.

The colors produced by iron and nickel, and also copper and other metallic salts, are destroyed by heating with nitric acid, while the color due to cobalt persists. Nickel, chromium, iron and copper interfere if present in concentrations greater than 0.1 M when only small quantities of cobalt are present.

**Determination of cobalt.** The red color which is obtained in the reaction between cobalt salts and nitroso-R-salt has been used by numerous investigators for the determination of small quantities of cobalt. This method has been particularly successful for determining cobalt in plant and animal tissues,<sup>5-10</sup> soils,<sup>11-13</sup> grasses<sup>14-15</sup> and also in steel<sup>16</sup> and carbides.<sup>22</sup>

The cobalt complex is usually formed in a hot acetic acid-acetate medium. After the color of the cobalt complex has thus been developed, hydrochloric or nitric acid is added to decompose the complexes of most of the other heavy metals. Iron and copper interfere if present other than in small amounts. Copper and ferric iron produce brown colors, and ferrous iron a green color. By a procedure described by Haywood and Wood,<sup>16</sup> however, interference due to iron can be eliminated (below). According to McNaught,<sup>7</sup> 100 $\gamma$  of copper does not interfere in the determination of 1 $\gamma$  of cobalt. Small quantities of nickel, manganese, titanium, vanadium and chromium are without effect. Cyanide, peroxide, persulfate and reducing agents must be absent.

The following procedure is recommended by McNaught.<sup>6</sup>

**Procedure.** If iron is present in appreciable quantities, remove by extracting as ferric chloride with ether from a 1:1 hydrochloric acid solution. Precipitate copper as cupric sulfide with hydrogen sulfide, filter and boil the filtrate to expel hydrogen sulfide.

The solution, or an aliquot part of it, should contain less than 20 $\gamma$  of cobalt. Evaporate nearly to dryness and add 1-2 ml. of concentrated nitric acid. Evaporate to dryness, and dissolve the residue in 10 ml. of water containing 0.5 ml. of 1:1 hydrochloric acid and 0.5 ml. of 1:10 nitric acid. Boil a few minutes to dissolve all solid material. Now add 2.0 ml. of a 0.1 per cent aqueous solution of nitroso-R-salt and 2.0 g. of hydrated sodium acetate. The pH of the solution should be approximately 5.5. This can be verified by testing with bromcresol green. Boil the mixture for 45 seconds and add 1.5 ml. of concentrated hydrochloric acid, and then boil for an additional 45 seconds. Cool the solution, dilute to a suitable volume, and determine the transmittancy at 510  $m\mu$ . By the standard series method of comparison, as little as 0.05 $\gamma$  of cobalt can be determined with tubes of 1-cm. diameter.

Marston and Dewey<sup>6</sup> have used nitroso-R-salt for the determination of cobalt in plant and animal tissues. Organic matter is first removed by treatment with nitric, sulfuric and perchloric acids, and the cobalt is then extracted with a chloroform solution of dithizone. After removing the water, acids, dithizone and chloroform, the residue is dissolved in 0.2 M citric acid and the cobalt caused to react with nitroso-R-salt in a sodium carbonate-buffered solution. The color is stabilized with nitric acid, and the color of the excess reagent is destroyed with bromine. The color of the cobalt complex is then compared with that of standards similarly prepared. By this procedure 2 $\gamma$  of cobalt can be recovered and estimated with an accuracy of within 1 per cent.

Haywood and Wood<sup>16</sup> have used nitroso-R-salt for the photometric determination of cobalt in steel. The colored cobalt complex is best obtained when all the free mineral acid is neutralized with sodium acetate. Interfering elements which are likely to occur in steel form complexes with the reagent which are destroyed by an excess of nitric acid. The following method is rapid, accurate, and gives reproducible results:

**Reagent.** *Nitroso-R-salt solution:* Dissolve 1 g. of nitroso-R-salt in 400 ml. of water, with warming if necessary, and then filter and dilute to 500 ml. with water.

*Standard cobalt solution:* Dissolve 0.4770 g. of  $\text{CoSO}_4$  in distilled water and dilute to 2 liters. Standardize this solution to contain 0.05 mg. of cobalt per ml.

**Procedure.** Dissolve 0.5 g. of steel in 20 ml. of a mixture of 150 parts of phosphoric acid ( $d = 1.75$ ), 150 parts of concentrated sulfuric acid and 700 parts of water. When the sample has dissolved, add 5 ml. of 6 N nitric acid and evaporate until fumes of sulfur trioxide appear. Cool and dilute by the careful addition of water to exactly 100 ml. Use a 10-ml. portion for the determination, and run both the unknown and a blank simultaneously as follows:

To 10 ml. of the solution to be analyzed, add 10 ml. of the reagent solution and 10 ml. of a sodium acetate solution containing 50 g. of sodium acetate per 100 ml. of solution. Heat to boiling and add 5 ml. of concentrated nitric acid, and then boil for at least 1, but not more than 2 minutes. Cool, dilute to 100 ml., and measure the absorption with a photoelectric absorptiometer, using spectrum blue filter No. 602. An empirical calibration graph is used to convert the instrument readings to per cent of cobalt.

**Determination of potassium.** Sideris<sup>17,18</sup> has used nitroso-R-salt for the colorimetric determination of small quantities of potassium in plant tissue. The method is based upon the precipitation of the potassium as  $K_2NaCo(NO_2)_6$ , and then estimating the potassium indirectly by determining the cobalt content of the precipitate with nitroso-R-salt.

**Reagent.** *Nitroso-R-salt:* Dissolve 1 g. of nitroso-R-salt in 70 ml. of water and add 30 ml. of iron-free acetone.

*Sodium acetate solution:* Dissolve 544.3 g. of sodium acetate trihydrate in sufficient water to make 1000 ml. of solution. Heat on a steam-bath and filter.

*Sodium cobaltinitrite solution:* Dissolve 12.5 g. of sodium cobaltinitrite in 100 ml. of water and filter. Immediately before using, mix portions of this reagent with equal volumes of 95 per cent alcohol.

*Standard cobalt solution:* Dissolve 3.043 g. of  $CoCl_2 \cdot 6H_2O$  in water, add 5 ml. of 5 N hydrochloric acid, and dilute with water to 1 liter. One ml. of this solution contains 0.7537 mg. of cobalt, and this is equivalent to 1.000 mg. of potassium. For the preparation of standards, aliquots of this solution are diluted from 100 to 500 times with water.

**Procedure.** Ash 0.5-1.0 g. of plant tissue, containing 0.04-0.10 mg. of potassium, in a platinum crucible, and dissolve the residue in 5 ml. of 1 per cent hydrochloric acid. Make alkaline to phenolphthalein by adding a few drops of 10 N sodium hydroxide and warm on a hot plate to precipitate iron and vanadium, which interfere with the potassium and cobalt determinations. Filter or centrifuge to remove the precipitate, and then dilute the filtrate or centrifugate to 100 ml. with water.

Place either 5 or 10 ml. of this solution in a 50-ml. beaker and neutralize, and then make distinctly acid with 1 ml. of 1 per cent hydrochloric acid. Evaporate to dryness on a steam-bath until all hydrochloric acid has been expelled. Allow the beaker to cool and add 0.5 ml. of water and 10 ml. of the sodium cobaltinitrite-alcohol reagent. Allow the mixture to stand in a refrigerator from 2-4 hours and filter through a fritted-glass crucible (Corning No. F), and wash the precipitate a number of times with an aqueous solution of 80-90 per cent iron-free acetone until the washings are no longer colored yellow by the sodium cobaltinitrite reagent. Rinse the outside of the crucible with water to remove any adhering drops of the cobaltinitrite reagent, and then place the crucible and contents in the beaker in which the potassium was originally precipitated. Add to the precipitate 5 ml. of 1 N sulfuric acid (if the quantity of the precipitate is large, add 10 ml. instead of 5 ml. of the sulfuric acid).

Carefully pour into the beaker, but outside of the crucible, sufficient water to half fill the beaker. Then warm on a steam-bath until the precipitate is dissolved. Remove the crucible from the beaker and rinse the external surface with a fine stream of water from a wash bottle and place the crucible in the mouth of a suction flask. Remove the solution in the pores of the crucible by several washings with small volumes of water, using suction. Transfer the solution in the suction flask and in the beaker to a 100-ml. volumetric flask and dilute to the mark with the washings from the beaker and the flask.

Place a 20-ml. aliquot of this solution in a graduated test tube and add 2 ml. of the sodium acetate solution and 1 ml. of the nitroso-R-salt solution. If the sample contains more than 15 $\gamma$  of potassium per ml., dilute a new aliquot to a convenient volume and treat 20 ml. of the diluted sample as directed above.

The ratio of the volumes of 1 N sulfuric acid and sodium acetate solution should be, in the final dilution, less than 1:2, since otherwise the red color of the complex cobalt salt will not develop. In those cases where the ratio is greater than 1:2, and the appearance of the red color is inhibited, add a few drops of 10 M sodium hydroxide solution to adjust the pH to approximately 8-10.

Measurements are made with a photoelectric colorimeter, employing a 10-mm. cell with a 7.5 mm. plunger, or a net depth of solution of 2.5 mm. can be used. Light filter No. 47 is recommended.

**Determination of iron.** Ferrous iron reacts with nitroso-R-salt at a pH range of 8-10 to form a green compound, the intensity of which is proportional to the iron content of the solution.<sup>2,19</sup> The sensitivity of this reaction is very great, and is capable of detecting quantities of iron ranging down to 0.2 $\gamma$  per ml. This reaction has been used by Sideris<sup>19</sup> for the colorimetric determination of iron in plant tissues. Hydroxylamine sulfate is used for reducing ferric iron to the ferrous state, and sodium acetate or ammonium hydroxide is suitable for adjusting the pH to the required value. Iron is determined by means of a photoelectric colorimeter with the use of appropriate light filters.

**Reagent. Nitroso-R-salt:** Place 0.5 g. of nitroso-R-salt in a 100-ml. volumetric flask containing 70 ml. of water, and dissolve by gentle shaking. Dilute to the mark with redistilled, iron-free acetone. This reagent is stable, and keeps for several months.

**Sodium acetate solution:** Place 544.3 g. of iron-free sodium acetate in 1000-ml volumetric flask, add 300 ml. of water, and shake gently while heating on a hot plate until solution is complete. Then dilute to the mark with water and filter.

**Standard iron solution:** Place 1 g. of pure iron in a 1000-ml. flask containing 10 ml. of concentrated sulfuric acid and 100 ml. of water and warm on a hot plate until dissolved. When solution is complete, cool, and dilute to volume with water. Suitable standards may be prepared by diluting this solution.

**Hydroxylamine sulfate solution:** Place 10 g. of hydroxylamine sulfate in a 100-ml. volumetric flask containing 80 ml. of water and shake until solution is complete. Then dilute to the mark with water.

**Procedure.** Ash about 5 g. of the dry plant tissue in a platinum crucible, and dissolve in 10 ml. of 10 per cent hydrochloric acid by gentle heating on a hot plate. Add approximately 20 ml. of water to the crucible and heat to about 90° C., and then transfer the solution quantitatively to a 100-ml. flask. Cool nearly to room temperature, dilute to the mark, and filter.

Place a 10-ml. aliquot of the solution in a test tube and neutralize with 5 N sodium hydroxide solution, using a very small piece of litmus paper as the indicator. Remove the paper with a glass rod, add 1 ml. of hydroxylamine sulfate solution, 1 ml. of nitroso-R-salt solution, and 2 ml. of sodium acetate solution. Dilute to 15 ml. in a graduated test tube and allow to stand for at least 20 minutes. Transfer the solution to a cell of a photoelectric colorimeter and determine the color intensity.

Recently Sideris and coworkers<sup>21</sup> have suggested the following improved modification of the original procedure:

**Procedure.** To a 10-ml. aliquot of the unknown in a 50-ml. Pyrex test tube, add 0.5 ml. of 10 per cent hydroxylamine sulfate and a drop of a 0.05 per cent aqueous solution of metanil yellow, and then neutralize by the dropwise addition of 14 per cent ammonium hydroxide to the appearance of a pinkish-yellow color. If the color is decidedly yellow, add 1 drop of 6 N hydrochloric acid. Then add to the mixture 1 ml. of 0.5 per cent nitroso-R-salt and 2 ml. of 4 N sodium acetate and dilute to a definite volume, in the range of 20 ml. Allow to stand 2-24 hours and determine the color intensity in the photoelectric colorimeter. Use filter KS-66 with transmission limits 640-700 m $\mu$  and a 2.5-mm. cell. A 10-mm. cell is recommended for concentrations below 1 $\gamma$  per ml. Good results are obtained with iron concentrations ranging up to 10 $\gamma$  per ml.

The green color formed by the iron compound in aqueous solutions is very stable and does not fade during a period of 48 hours under ordinary laboratory conditions.

Cobalt interferes with this determination by forming a wine-red color with the reagent. Copper and nickel give a yellowish-brown color. This color, however, forms only at pH values lower than 7, and almost disappears at the pH range suitable for the development of the color between nitroso-R-salt and iron. The color produced by cobalt can be eliminated in the same way, but cobalt may not occur in plants in sufficient quantity to cause interference in the determination of iron by this method.

The sensitivity of the nitroso-R-salt method for iron compares favorably with that of the 1,10-phenanthroline or the 2,2'-dipyridyl methods, and the green color of the nitroso-R-salt compound with iron is better suited for colorimetric measurements than the pink color obtained by the other two methods.

**Salts of nitroso-R-salt.** Bernardi and Schwartz<sup>20</sup> have studied the reaction of nitroso-R-salt with a number of cations and report the formation of a number of salts. These are shown in Table 63.

TABLE 63.

Inorganic Salt Used	Compound	Remarks
Pb(NO <sub>3</sub> ) <sub>2</sub>	(C <sub>10</sub> H <sub>8</sub> O <sub>8</sub> NS <sub>2</sub> Na <sub>2</sub> ) <sub>2</sub> · Pb · Pb(NO <sub>3</sub> ) <sub>2</sub>	Red
AgNO <sub>3</sub>	(C <sub>10</sub> H <sub>8</sub> O <sub>8</sub> NS <sub>2</sub> Na <sub>2</sub> ) <sub>2</sub> · Ag · AgNO <sub>3</sub> · 8H <sub>2</sub> O	Lemon yellow
BaCl <sub>2</sub>	(C <sub>10</sub> H <sub>8</sub> O <sub>8</sub> NS <sub>2</sub> Na <sub>2</sub> ) <sub>2</sub> · Ba · BaCl <sub>2</sub> · 6H <sub>2</sub> O	Orange
CaCl <sub>2</sub>	(C <sub>10</sub> H <sub>8</sub> O <sub>8</sub> NS <sub>2</sub> Na <sub>2</sub> ) <sub>2</sub> · Ca · CaCl <sub>2</sub>	Green

The barium salt is insoluble in hydrochloric acid and in ethyl alcohol, while the calcium salt is soluble in hydrochloric acid but is insoluble in ethyl alcohol and in ammonium hydroxide. This suggests a possible method for separating barium and calcium.

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***p*-NITROSOTHYMOL**

Synonym: 6-Nitroso-3-hydroxy-1-methyl-4-isopropylbenzene

 $C_{10}H_{13}O_2N$ 

Mol. Wt. 179.21

Beil. Ref. VII, 664 (359).

**Use:** Detection and determination of alkali carbonates.

*p*-Nitrosothymol is obtained as needles from chloroform. It melts with slight decomposition when slowly heated to 160-164° C. It is slightly soluble in boiling water and is easily soluble in ether and chloroform.

**Preparation:** Dissolve 100 g. of thymol in 500 ml. of 95 per cent ethyl alcohol and add 500 ml. of concentrated hydrochloric acid cooled to 0° C. To this solution add 72 g. of commercial sodium nitrite in portions of about 5 g. each, and stir well during the addition. After half of the nitrite has been added, the mass becomes thick and must be stirred more vigorously, and the time between the additions must be increased. When all of the nitrite has been added, transfer the mixture to a 12 l. flask containing 8 l. of cold water. Mix well, filter off the yellow precipitate with suction, wash well with water, dry, and recrystallize the crude product from benzene.<sup>1,2</sup>

**Detection of alkali carbonate in the presence of alkali bicarbonate.** During a study of the tautomerism of *p*-nitrosothymol and thymoquinonemonoxime, Sumerford and Hartung<sup>3</sup> observed that a solution of sodium carbonate was sufficiently alkaline to tautomerize the colorless *p*-nitrosothymol into thymoquinonemonoxime with the formation of a red color due to the presence of the anion of the sodium salt of the oxime.

Under the same conditions sodium bicarbonate produces no color, or only a very faint yellow color, depending upon the quantity of carbonate contained in the bicarbonate sample. Thus *p*-nitrosothymol can be used to distinguish between alkali carbonates and bicarbonates, and provides a method for detecting the presence of an alkali carbonate in a sample of an alkali bicarbonate.<sup>4</sup>

**Procedure.** Place the solution to be tested in a Nessler tube and add an excess of a 0.35 M solution of *p*-nitrosothymol in neutral acetone or neutral dioxane. Shake for 10-15 minutes and filter off the excess *p*-nitrosothymol. By comparing the resulting color with that obtained with a blank test, a solution 0.001 M in sodium carbonate can be detected with the unaided eye.

By comparing the color produced with a solution of a carbonate and *p*-nitrosothymol with colors produced in standards containing known quantities of carbonate, this reaction may be used for the quantitative determination of small quantities of carbonates. The method is accurate and the results are reproducible if the conditions for mixing the bicarbonate solution are made the same as those under which the reference standards are prepared from known alkali carbonate solutions and *p*-nitrosothymol.

1. R. Schiff, *Ber.* **8**, 1500 (1875).

2. *Organic Synthesis*, Collective Vol. I, 2nd ed., p. 511, John Wiley, New York (1941).

3. W. T. Sumerford and W. H. Hartung, *J. Am. Pharm. Assn.* **24**, 65 (1940).

4. W. T. Sumerford, D. Dalton and R. Johnson, *Ind. Eng. Chem., Anal. Ed.* **15**, 38-39 (1943); *C.A.* **37**, 1099 (1943).

## CHAPTER XII

### MISCELLANEOUS OXIMES

The salt-forming characteristics of the oximes have suggested their use as precipitants for various metals. Copper, cobalt, nickel, iron and other metals form salts with many oximes, although these compounds are not generally superior as reagents for these metals.<sup>1-5</sup>

1. F. Feigl, *Chem. Weekblad.* **27**, 110-4 (1930); *C.A.* **24**, 3192 (1930).
2. J. V. Dubsky, Fr. Brychta and M. Kuras, *Pub. faculte sci. univ. Masaryk* **129**, 1-26 (1931); *C.A.* **26**, 2943 (1932).
3. J. V. Dubsky and M. Kuras, *Spisy Vydavane prirodovedeckou Fakultou Masarykovy Univ.* **114**, 43 pp. (1929); *C.A.* **24**, 4733 (1930).
4. W. Hieber and F. Leutert, *Ber.* **62B**, 1839-46 (1929); *C.A.* **23**, 4692 (1929).
5. W. Hieber and F. Leutert, *Ber.* **60B**, 2296-310 (1927); *C.A.* **22**, 3104 (1928).

#### ACETALDOXIME

$C_2H_5ON$

Mol. Wt. 59.07

Beil. Ref. I, 608.

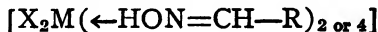


**Use:** Detection of cobalt, copper, and nickel.

Acetaldoxime is a white, crystalline solid. It melts at 47° C. and boils at 115° C. Its sp. gr. is 0.966. It is very soluble in water, alcohol, and ether.

**Preparation:** Dissolve 32.5 g of hydroxylamine hydrochloride and 25.5 g. of sodium carbonate in 90 ml. of water and cool, and add this solution to a cooled mixture of 20 g. of acetaldehyde and 10 g. of water. Allow to stand for a time and extract with ether. Dry the ether solution with calcium chloride and finally evaporate the ether on a water bath. The reagent boils at 114-115° C.<sup>1</sup>

**Reactions.** Aldoximes react with cobalt, copper, and nickel salts to form compounds of the general formula



in which X is a halogen and M a metal. These compounds are obtained by the direct crystallization from alcoholic solutions of the oxime and metal halides.<sup>2</sup> Violet-red prisms are obtained from a solution of 2.4 g. of  $CoCl_2 \cdot 6H_2O$  and 2.4 g. of acetaldoxime in alcohol. This compound is soluble in water and chloroform with the formation of a bright-red color, and in alcohol, acetone and ethyl acetate to form a blue color. The formula for this compound is  $4CH_3-CH=NOH \cdot CoCl_2$ .

The nickel compound,  $4CH_3-CH=NOH \cdot NiCl_2$ , formed in the same way, is bright blue in color.

The compound  $2\text{CH}_3\text{—CH=NOH}\cdot\text{CuCl}_2$  is formed when a concentrated alcoholic solution of 1.2 g. of acetaldoxime is added to a concentrated alcoholic solution of 2.4 g. of  $\text{CuCl}_2\cdot 6\text{H}_2\text{O}$ . After a time this compound separates as bright blue, glistening leaves. It is readily soluble in water and acetone, but is only slightly soluble in alcohol.

1. J. Petraczek, *Ber.* 15, 2784 (1882).
2. W. Hieber and F. Leutert, *Ber.* 60B, 2296-310 (1927); *C.A.* 22, 3104 (1928).

### ACETONEDICARBOXYLIC ACID OXIME

$\text{C}_5\text{H}_7\text{O}_5\text{N}$

Mol. Wt. 161.11

Beil. Ref. III, 796.



**Use:** Detection of cobalt, copper, iron, lead, mercury and silver.

This reagent is a crystalline solid, melting at  $53\text{--}4^\circ\text{C}$ .

**Preparation:** Mix an aqueous solution of hydroxylamine with an aqueous solution of acetonedicarboxylic acid, and allow to stand 12 hours. Shake out with ether. Large crystals of the reagent are obtained when the ether solution is evaporated.<sup>1</sup>

**Reactions.** Acetonedicarboxylic acid oxime reacts with cupric acetate and ammonia to yield green, slightly characteristic needles. Ferrous ammonium sulfate gives a brownish-green, and ferric chloride a deep blue compound. With cobalt chloride and ammonia, an amorphous, green salt of the following composition is obtained,  $\text{HOCO—ON}=\text{C}=(\text{CH}_2\text{—CO}_2\text{—CoOH})_2$ .

Lead acetate gives an orange color, silver nitrate and sodium acetate a yellow turbidity, and mercurous nitrate orange needles.<sup>2</sup>

1. W. O. Emery, *Ber.* 23, 3765 (1890).
2. J. V. Dubsky, Fr. Brychta and M. Kuras, *Pub. faculte sci. univ. Masaryk.* 129, 1-26 (1931); *C.A.* 26, 2943 (1932).

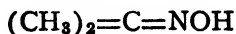
### ACETONEOXIME

Synonym: Acetoxime

$\text{C}_3\text{H}_7\text{ON}$

Mol. Wt. 73.09

Beil. Ref. I, 649.



**Use:** Detection of cobalt.

Acetoneoxime occurs as prisms, having a melting point of  $59\text{--}60^\circ\text{C}$ . and a density of 0.97. The compound is extremely soluble in water, alcohol, and ether. It reacts neutral.

**Preparation:** In a small flask, place a solution of 5 g. of hydroxylamine hydrochloride in 10 ml. of water, and to this add 3 g. of sodium hydroxide dissolved in 10 ml. of water. To this mixture, slowly add with shaking, 7.6 ml.

of pure acetone. Stopper the flask and allow to stand 24 hours. Test a few drops of the mixture for free hydroxylamine with Fehling's solution. If no hydroxylamine is present, shake the liquid with an equal volume of ether to separate the oxime. Separate the ether layer and repeat the extraction with fresh ether. Combine the extracts and filter through dry paper into a distilling flask. Distill most of the ether and pour the remainder of the solution into a crystallizing dish and allow to stand until all of the ether has evaporated. Remove the last traces of the ether by heating a few minutes on a water bath, and recrystallize the residue from petroleum ether.<sup>1</sup>

**Detection of cobalt.** Suspensions of water-free cobalt chloride in an inert solvent, such as chloroform, ether or ethylene bromide are colored a corn-flower blue by the addition of a crystal of acetoneoxime. This reaction may be used for the detection of small quantities of cobalt.<sup>2</sup>

**Procedure.** Evaporate material to be tested to dryness with hydrochloric acid, and then grind the residue to a fine powder with 1-2 ml. of chloroform. To the suspension thus prepared, add a crystal of acetoneoxime. A blue color indicates cobalt. It is essential that the material be finely ground and water-free.

The color is obtained if 1 g. of the material to be tested contains only 0.05 mg. of cobalt.

Nickel chloride does not interfere, but nickel bromide and nitrate color the chloroform green; hence, the reaction is reliable only when the chloride is used. Cupric halides are reduced with the reagent. The blue color of cobalt disappears immediately upon the addition of copper or zinc.

The composition of the cobalt compound corresponds to 1 mole of the oxime to 2 moles of cobalt chloride.

1. V. Meyer and Fanin, *Ber.* 15, 1324 (1882).

2. W. Hieber and F. Leutert, *Ber.* 60B, 2310-7 (1927); *C.A.* 22, 3105 (1928).

## AMINOACETOXIME

$C_3H_5ON_2$

Mol. Wt. 88.09



**Use:** Detection of copper and iron.

This compound cannot be isolated in the pure form, although it is very stable in alcoholic and aqueous solutions.

**Preparation.** Aminoacetoxime is prepared by the action of hydroxylamine hydrochloride on aminoacetone.<sup>1</sup>

**Reaction with copper and iron.** An alcoholic solution of aminoacetoxime reacts with copper acetate to yield a copper salt.

This compound is light green in color, but dissolves in ammonia with the formation of a violet solution.

Aminoacetoxime reacts with ferric chloride to give a brown-red color, and with ferrous ammonium sulfate to give an orange-red color.<sup>2</sup>

1. *Chem. Zentr.* II, 415 (1931).

2. J. V. Dubsky, Fr. Brychta, and M. Kuras, *Pub. faculte sci. univ. Masaryk.* 129, 1-26 (1931); *C.A.* 26, 2943 (1932).

### $\alpha$ -BENZALDOXIME

Synonym: Benz-*anti*-aldoxime

$C_7H_7ON$

Mol. Wt. 121.13

Beil. Ref. VII, 218.

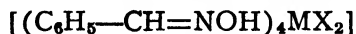


**Use:** Detection of cobalt and nickel.

$\alpha$ -Benzaldoxime consists of colorless needles, melting at 34-35° C. It boils at 122-124° C. at 12 mm.

**Preparation:** Add 21 g. of benzaldehyde to a solution prepared by dissolving 14 g. of sodium hydroxide in 40 ml. of water, and then add slowly 15 g. of hydroxylamine hydrochloride with constant shaking. The mixture becomes warm during the reaction, and upon cooling a crystalline mass of the sodium salt of benzaldoxime forms. Add sufficient water to form a clear solution, and through this pass a stream of carbon dioxide. A colorless emulsion of  $\alpha$ -benzaldoxime separates on the surface of the liquid and is extracted with ether. The ether extract is dehydrated by shaking with anhydrous sodium sulfate, and the ether is then removed on the water-bath. Purify the impure product by pouring into a solution prepared by dissolving 5 g. of sodium in 60 ml. of alcohol, from which the aldoxime separates as the sodium salt as a semi-solid mass. Filter and wash with a saturated solution of sodium ethoxide in alcohol to dissolve the  $\beta$ -oxime. Dissolve the residue in water, saturate with carbon dioxide, and extract with ether as before. Air is then drawn through the liquid to remove the last traces of ether. The oxime, if pure, solidifies upon cooling to 0° C. If the oxime does not solidify, distill *in vacuo*. The compound boils at 122-124° C. at 12 mm.<sup>1</sup>

**Reactions with cobalt and nickel.**  $\alpha$ -Benzaldoxime reacts with cobalt and nickel chlorides and bromides to form compounds of the general formula



in which X represents either bromide or chloride and M is cobalt or nickel. The nitrogen of the oxime group is coordinated to the metal atom. When a solution of 0.6 g. of cobalt chloride and 2.4 g. of  $\alpha$ -benzaldoxime in alcohol is evaporated at ordinary temperature a red-brown, crystalline cobalt compound is formed. A solution of 0.8 g. of nickel chloride and 1.6 g. of  $\alpha$ -benzaldoxime in alcohol upon evaporation at room temperature yields the blue-green nickel compound.<sup>2</sup>

1. E. Beckmann, *Ber.* 23, 1684 (1890).

2. W. Hieber and F. Leutert, *Ber.* 60B, 2296-310 (1927); *C.A.* 22, 3104 (1928).

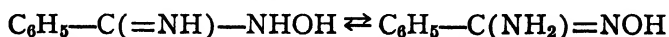
**BENZAMIDOXIME**

Synonym: Benzenylamidoxime

 $C_7H_8ON_2$ 

Mol. Wt. 136.13

Beil. Ref. IX, 304.

**Use:** Detection of copper, iron, lead and nickel.

Benzamidoxime is a crystalline solid melting at 79-80° C. It is slightly soluble in cold water, but is easily soluble in alcohol, ether, chloroform and benzene.

**Preparation:** Mix an alcoholic solution of 1 molecular weight of hydroxylamine hydrochloride with an equivalent quantity of an aqueous solution of sodium carbonate. To this add 1 molecular weight of benzonitrile and as much alcohol as is required to form a clear solution. Heat the mixture for 18 hours at 80° C. Crystallize the precipitate from water and purify by repeated solution in benzene and precipitation with ligroin.<sup>1</sup>

**Reactions with metals.** Dubsky and Kuras<sup>2</sup> have studied the reaction of benzamidoxime with solutions of a number of metallic salts. Trivalent nickel reacts to form a reddish-violet salt. Copper reacts to form three compounds: an olive green monohydrate,  $[C_6H_5-C(NH_2)-NO-CuOH] \cdot H_2O$ , a black green salt with 5 molecules of water of hydration, and a black salt with 8 molecules of water.

Lead forms a white salt, and ferric iron a red salt.

1. T. Tiemann and P. Kruger, *Ber.* 17, 1685 (1884).
2. J. V. Dubsky and M. Kuras, *Spisy Vydavane prirodovedeckou Fakultou Masarykovy Univ.* 114, 43 pp. (1929); *C.A.* 24, 4733 (1930).

**CINNAMALANISALACETONE OXIME** $C_{20}H_{19}O_2N$ 

Mol. Wt. 305.35

**Use:** Detection and determination of tungsten.

Cinnamalanisalacetone oxime precipitates tungsten quantitatively from a hydrochloric acid solution as a bright yellow precipitate, which is satisfactory for the gravimetric determination of tungsten. This reagent appears to be specific for the tungstate ion, and offers considerable promise as a reagent for the determination of tungstates.

1. J. H. Yoe, *Va. J. Sci.* 3, 8-10 (1942).

**CINNAMALDOXIME** $C_9H_9ON$ 

Mol. Wt. 147.16

Beil. Ref. VII, 356.

**Use:** Detection of cobalt and copper.

This compound exists in two forms, *syn*-cinnamaldoxime and *anti*-cinnamaldoxime.

*syn*-Cinnamaldoxime is obtained as glistening needles from benzene and water. It melts at 138.5° C. It is almost insoluble in water, and is only slightly soluble in alcohol, ether, chloroform and in alkalis.

**Preparation:** Suspend cinnamaldehyde in concentrated sodium hydroxide, and to this mixture add, with moderate heating, 1.5 times as much hydroxylamine hydrochloride. The solution becomes clear and light yellow after standing for a short time. Allow to stand 24 hours, and precipitate the isomeric cinnamaldoximes by means of carbon dioxide. Wash with water and dry. *anti*-Cinnamaldoxime is extracted by treating the mixture with ligroin (B.P. = 40-70° C.). This compound separates on cooling and can be converted to *syn*-cinnamaldoxime by treating an ether solution with hydrogen chloride gas.

*syn*-Cinnamaldoxime, which remains behind after the extraction of the *anti*-compound, can be purified by crystallization from boiling benzene.<sup>1</sup>

**Reaction with cobalt and copper.** A reddish-brown compound, having the composition,  $C_6H_5-CH=CH-CH=NOH \cdot CoCl_2$  is formed when a solution of 1 g. of cobalt chloride in absolute alcohol is mixed with an alcoholic solution containing 4.8 g. of *anti*-cinnamaldoxime.

When an alcoholic solution containing 1 g. of cupric chloride is mixed with an alcoholic solution containing 1.2 g. of cinnamaldoxime, a crystalline compound of the following composition,  $2C_6H_5-CH=CH-CH=NOH \cdot CuCl_2$ , is formed.

The *syn*-isomer yields a dirty blue-violet solution with cobalt salts. The product is not crystalline at first, but after repeated evaporation with alcohol, red-brown crystals of the *anti*-compound are formed.<sup>2</sup>

1. E. Bamberger and C. Goldschmidt, *Ber.* 27, 3428 (1894).

2. W. Hieber and F. Leutert, *Ber.* 60B, 2296-310 (1927); *C.A.* 22, 3104 (1928).

## DIAMINOACETOXIME

$C_3H_9ON_3$

Mol. Wt. 103.10



**Use:** Detection of cobalt, copper, and iron.

**Preparation:** Prepare diaminoacetone by adding gradually with cooling and shaking, 11.6 g. of powdered diisonitrosoacetone to a solution of 135 g. of zinc chloride in 180 ml. of hydrochloric acid ( $d = 1.19$ ). Allow the mixture to stand 2 days, dissolve 20 g. of the zinc double salt in a mixture of 250 ml. of hot water and 15 ml. of concentrated hydrochloric acid, and then treat with hydrogen sulfide to precipitate the zinc. Convert the diaminoacetone hydrochloride remaining in the solution to diaminoacetoxime by the action of hydroxylamine hydrochloride.<sup>1</sup>

**Reactions.** Diaminoacetoxime yields a black microcrystalline copper salt of unknown composition. With cupric acetate, a rose-violet compound is

obtained, which becomes blue-violet upon addition of ammonia. Ferrous ammonium sulfate gives a yellowish-brown compound, which is converted to red-brown insoluble needles upon treatment with ammonia. Ferric chloride and ammonium hydroxide yield a red color with the reagent. Cobalt chloride gives an orange compound, which turns to a brownish-red in the presence of ammonia.<sup>2</sup>

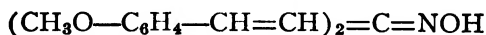
1. G. Kalischer, *Ber.* **28**, 1520 (1895).

2. J. V. Dubsky, Fr. Brychta and M. Kuras, *Pub. faculte sci. univ. Masaryk.* **129**, 1-26 (1931); *C.A.* **26**, 2943 (1932).

## DIANISALACETONE OXIME

$C_{19}H_{19}O_3N$

Mol. Wt. 309.34



**Use:** Detection and determination of tungsten.

Dianisalacetone oxime precipitates tungsten quantitatively from a hydrochloric acid solution as a bright yellow precipitate, which is satisfactory for the gravimetric determination of tungsten. This reagent appears to be specific for the tungstate ion, and offers considerable promise as a reagent for the determination of tungstates.

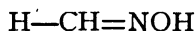
1. J. H. Yoe, *Va. J. Sci.* **3**, 8-10 (1942).

## FORMALDOXIME

$CH_3ON$

Mol. Wt. 45.04

Beil. Ref. I, 590.



**Use:** Detection of copper, manganese, and nickel.

Determination of copper, manganese and nickel.

Formaldoxime is a colorless liquid, boiling at 84° C. It polymerizes gradually at ordinary temperatures to form a gel. In aqueous solutions it is stable at ordinary temperature if the concentration is 10-20 per cent.

**Preparation:** A solution of formaldoxime, suitable for use as a reagent in the following procedures, may be prepared by dissolving 2 g. of hydroxylamine hydrochloride and 1 ml. of 40 per cent formaldehyde in 50 ml. of water.<sup>1</sup> The reagent may also be prepared by boiling 3 g. of trioxymethylene, 7 g. of hydroxylamine hydrochloride and 15 ml. of water, until the mixture is clear.<sup>2</sup>

**Reactions.** Formaldoxime reacts with manganese, nickel, cobalt, ferric and cupric ions to give color reactions which may be used to detect these substances. The following procedure is used:<sup>3</sup>

**Procedure.** To 10 ml. of a solution of manganese, nickel, cobalt, iron or copper salt containing 10 mg. of the cation per liter of solution, add 1 drop



of the above reagent, mix well, and add 2 drops of 10 N sodium hydroxide solution and again mix. The following results are obtained:

(a) *Manganese*: A reddish-orange precipitate forms instantly, and this persists on heating over a boiling water bath for 15 minutes.

(b) *Nickel*: An orange-yellow precipitate forms which persists in the cold for several hours, but which dissolves on heating over a boiling water bath for 5 minutes.

(c) *Cobalt*: A pale yellow precipitate forms, which is stable in hot or cold solution.

(d) *Iron*: After 2-3 minutes a violet-red color appears. This develops to a maximum during a period of about 12 hours. The color disappears completely after heating for 2 minutes on a boiling water-bath.

(e) *Copper*: A violet coloration appears, which is discharged after 12-13 hours in cold, or within 2 minutes at 100° C.

The sensitivities of these reactions are given in Table 64.<sup>2</sup>

TABLE 64.

Metal	Sensitivity mg. per liter
Manganese .....	0.05
Nickel .....	0.1
Cobalt .....	0.2
Iron .....	0.1
Copper .....	0.1

**Detection of manganese.** The purple color which forms when formal-doxime is added to an alkaline solution of a manganese salt may be used for the detection and determination of manganese. By this reaction manganese may be detected in different valence states at a concentration of 0.02 mg. per liter. Iron interferes and must be precipitated with zinc hydroxide.<sup>1,4,5</sup>

**Determination of manganese.** Small quantities of manganese may be determined colorimetrically by means of the purple color which is formed when formal-doxime is added to alkaline solutions of manganese salts.

**Reagent.** Mix 3 g. of trioxymethylene, 7 g. hydroxylamine and 15 ml. of water, and slowly bring the mixture to boiling. Boil until the liquid is clear, and then allow to cool.

**Procedure.** Manganese may be determined in 10 ml. of water by adding a drop of the above reagent and four drops of N sodium hydroxide, and comparing the resulting color with that obtained with standards of known manganese concentration. The sensitivity of this reaction is 0.08 mg. per liter.<sup>6</sup>

Iron interferes with this procedure and must be oxidized to the ferric state and removed. In determining manganese in water, any turbidity arising from calcium or magnesium is eliminated by the addition of a little ammonium chloride.

A similar method may be used to determine manganese in iron after dissolving the sample in acid and removing the iron. Cruelas and Valetto<sup>7</sup> have determined manganese in the presence of iron by precipitating the iron with zinc oxide. The color is produced in the manganese solution by adding the formaldoxime reagent, and then measuring the color with the aid of a Pulfrich photometer with No. 2 blue and No. 4 yellow glasses. Interference by nickel, cobalt or copper can be prevented by the addition of a small quantity of alkaline sodium cyanide.

Sideris<sup>9</sup> has studied the determination of manganese in the presence of iron, and has found that a purple color is obtained with iron which to some extent interferes with the observation of the wine-red color produced when the reagent reacts with manganese. A study of the conditions influencing the development of the color produced with formaldoxime and ferric iron shows that oxygen and time are essential factors. The addition of either ammonium tartrate or sodium cyanide tends to stop the reaction with iron, but a faint yellowish-green color is obtained which interferes somewhat. If, however, the same quantity of iron present in the sample to be analyzed is added to the standard solution used in the comparison, the above colorimetric determination is suitable for determining 0.025-20% of manganese with an accuracy of 5-15 per cent. The following procedure for determining small quantities of manganese in plant tissues has been suggested by Sideris.<sup>9</sup>

**Reagent.** Mix 47 g. of hydroxylamine sulfate and 20 g. of trioxymethylene with 100 ml. of distilled water and boil until clear.

**Procedure.** Ash a quantity of plant tissue containing 0.01-0.05 mg. or more of manganese, and make certain that all iron is oxidized to the ferric state during the ashing process. Dissolve the ash in 2-5 ml. of 0.077 N hydrochloric acid, filter, wash the filter paper with water, and dilute the solution to 25 ml. If the solution contains more than 0.02 mg. of manganese per ml., further dilution is necessary. Next determine iron with 1,10-phenanthroline by the method of Saywell and Cunningham<sup>10</sup> and proceed as follows:

Add 0.52 ml. (about 5 drops) of 40 per cent potassium hydroxide to 10 ml. of the solution to be analyzed and stir well. Then add 0.5 ml. of 20 per cent sodium cyanide. Mix again and add 3 drops of formaldoxime reagent and again stir. The intensity of the wine-red color which develops is directly proportional to the manganese content of the solution. Compare this color with that of standards similarly prepared and containing respectively 0.002, 0.008, and 0.012 mg. of manganese per ml. These standard solutions must contain approximately the same amount of iron as the unknown, and this is accomplished by adding the proper quantity of a standard ferric chloride solution. Add 0.5 ml. of a 5 per cent solution of gum ghatti to the unknown and to the standard solutions. Allow to stand for 20 minutes and read in a colorimeter.

Wiese and Johnson<sup>11</sup> report that in determining manganese in blood, bones, and similar materials, the above procedure is unsuitable because the precipitation is carried out in an alkaline solution, thus causing the precipitation of phosphates, which mask and adsorb the color. This has been confirmed by Sideris,<sup>12</sup> but according to a modified procedure proposed by him, phosphates can be removed by precipitation with 5 per cent lead acetate solution, and the excess of lead may then be precipitated with a 20 per cent sodium sulfate solution. Using this modified method, 10 ml. of a solution containing 0.005-0.01 mg. of manganese and 0.01-0.1 mg. of phosphate may be analyzed with an average error of only 2 per cent.<sup>12</sup>

Small quantities of manganese can be determined in the presence of as high as 99.5 per cent of cobalt by a procedure which depends upon the separation of manganese as manganese ammonium phosphate,  $\text{MnNH}_4\text{PO}_4$ , followed by the conversion of the manganese to the manganese formaldoxime compound, which can be determined colorimetrically.<sup>13</sup>

Excellent results have been reported in determining manganese by a modified Deniges method.<sup>1,8</sup>

**Detection and determination of nickel.** A green to yellow color is obtained when formaldoxime is added to an alkaline solution of a nickel salt. This color reaction may be used for the detection and determination of nickel. Deniges<sup>14</sup> has used this reagent for the detection and determination of nickel in commercial samples of cobalt salts.

**Reagent.** Mix 3 g. of trioxymethylene and 7 g. hydroxylamine hydrochloride with 15 ml. of water, and boil until clear.

**Procedure.** Place in a tube 20 ml. of a solution of a cobalt salt to be analyzed containing approximately 50 mg. of cobalt per liter of solution, and in another tube place 20 ml. of a solution of a nickel-free cobalt salt of about the same cobalt concentration as that of the unknown solution. To each tube add 2 drops of the formaldoxime reagent. Mix and add 4 drops of 10 N sodium hydroxide, and again mix. If nickel is present in the unknown sample, a brownish tint appears. By this reaction as little as 0.1 per cent of nickel in a cobalt salt can be detected.

This method may also be used for the colorimetric determination of nickel in cobalt salts.

Fischer and Cayard<sup>15</sup> have used similar procedure to determine small quantities of nickel in silver.

Wenger, Duckert and Busset,<sup>16</sup> in a critical review of the methods for detecting nickel, recommend the use of formaldoxime for a test tube reaction for nickel.

**Detection and determination of copper.** An intense violet color is obtained when formaldoxime is added to a very dilute solution of copper sulfate that has been made alkaline with potassium hydroxide. This color is detectable at a dilution of 1:1,000,000. This is a more sensitive reaction than the well-known Biuret test. The color is discharged by the action of carbon dioxide of

the air. Nickel interferes, causing a darker color.<sup>17</sup> Copper may be determined colorimetrically by means this reaction in the absence of interfering substances.<sup>6</sup>

1. E. Kahane, *Ann. chim. anal. chim. appl.* **17**, 175-8 (1935); *C.A.* **29**, 5376 (1935).
2. G. Deniges, *Compt. rend.* **194**, 895-7 (1932); *C.A.* **26**, 2935 (1932).
3. G. Deniges, *Bull. soc. pharm. Bordeaux.* **70**, 101-6 (1932); *C.A.* **27**, 927 (1933).
4. P. Wenger, R. Duckert, and M. Busset, *Helv. Chim. Acta.* **24**, 1143-50 (1941); *C.A.* **36**, 3450 (1942).
5. J. V. Dubsky and A. Langer, *Chem. Obzor.* **15**, 11-12 (1940); *C.A.* **36**, 2810 (1942).
6. G. H. Wagenaar, *Pharm. Weekblad.* **75**, 641-8 (1938); *C.A.* **32**, 6573 (1938).
7. J. Cruellas and R. Valetto, *Anales soc. cien. Argentina.* **126**, 89-91 (1938); *C.A.* **33**, 2064 (1939).
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13. L. Waldbauer and N. M. Ward, *Ind. Eng. Chem., Anal. Ed.* **14**, 727-8 (1942); *C.A.* **36**, 6435 (1942).
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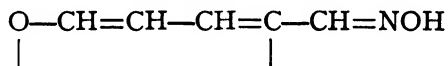
### $\beta$ -FURFURALOXIME

Synonym:  $\beta$ -Furfuraldoxime

$C_5H_5O_2N$

Mol. Wt. 111.10

Beil. Ref. XVII, 281.



**Use:** Determination of palladium:

This reagent crystallizes as needles from ligroin. It melts at 91-92° C. and boils with decomposition at 201-8° C. It is only slightly soluble in cold water, but dissolves readily in alcohol, ether, carbon disulfide, benzene, and acetic acid.

**Preparation:** Dissolve 10 g. of hydroxylamine hydrochloride in 40 ml. of methyl alcohol, and add 19.5 g. of crystalline sodium acetate in 40 ml. of dilute alcohol. Add 12 g. of furfural. Allow the mixture to stand 24 hours, and filter off the precipitated sodium chloride. Evaporate in a vacuum at room temperature to a volume of about 30 ml., and pour into 70 ml. of water. Crystallize the precipitated  $\beta$ -oxime 3 times from 10 per cent alcohol with the addition of animal charcoal.<sup>1,2</sup>

**Determination of palladium.**  $\beta$ -Furfuraloxime reacts with solutions of palladium salts to form a light yellow precipitate. Precipitation is quantitative, and may be used for the gravimetric determination of palladium.<sup>3,4</sup>

**Reagent.** Shortly before use, dissolve 10 g. of  $\beta$ -furfuraloxime in 100 ml. of alcohol.

**Procedure.** Dilute the solution containing about 30 mg. of palladium to 100 ml., and adjust the acidity to about 0.36 N in hydrochloric acid. Then add 2 ml. of a 10 per cent solution of the reagent. Palladium is completely precipitated as a curdy, light yellow compound having the composition  $\text{Pd}(\text{C}_4\text{H}_3\text{—O—CH=NOH})_2\text{Cl}$ . Wash this precipitate, first with 50 ml. of cold, 1 per cent hydrochloric acid, and then with 50 ml. of water, and finally dry for 2 hours at a temperature not exceeding  $110^\circ\text{C}$ . Filter through a Gooch crucible and weigh. The factor for palladium is 0.2669.

By the above procedure palladium can be determined in the presence of platinum, ruthenium, rhodium, iridium, iron, cobalt, nickel, copper, manganese, mercury, zinc, aluminum, antimony, bismuth, tin, cadmium, calcium, strontium, barium, magnesium, sodium, potassium, chromium, thorium, titanium, zirconium, molybdenum, vanadium, tungsten, phosphate, arsenate, borate, selenite, sulfate, and nitrate. Gold, silver, mercurous, lead, and ceric ions, however, interfere in the above procedure.

The precipitate produced with the reagent and palladium is more easily handled than that with dimethylglyoxime, and the excess reagent is more soluble. The results obtained with  $\beta$ -furfuraloxime are somewhat more satisfactory, since the molecular weight is greater than the compound obtained with dimethylglyoxime.

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2. O. L. Brady and R. F. Goldstein, *J. Chem. Soc.* **130**, 1961 (1927).
3. J. R. Hayes and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.* **14**, 491-3 (1942); *C.A.* **36**, 4052 (1942).
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## ISATIN- $\beta$ -OXIME

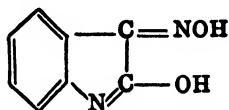
$\text{C}_8\text{H}_6\text{O}_2\text{N}_2$

Mol. Wt. 162.13

Beil. Ref. XXI, 443(353).

**Use:** Detection of cobalt, copper, iron, lead, nickel, silver and uranium.

Determination of uranium.



Isatin- $\beta$ -oxime consists of golden-yellow needles, melting at  $202^\circ\text{C}$ . It is very slightly soluble in water, more soluble in ethyl alcohol, and only slightly soluble in ether.

**Preparation:** Mix 1 mole of isatin and 1 mole of hydroxylamine hydrochloride and 0.5 moles of sodium carbonate, and allow the mixture to stand in a water-alcohol mixture for a few hours. Add water to precipitate the orange-

red needles, and crystallize the precipitate from a mixture consisting of equal volumes of alcohol and water.<sup>1</sup>

**Reactions with metals.** Hovorka and Sykora<sup>2</sup> have used a 1 per cent alcoholic solution of isatin- $\beta$ -oxime to detect mercury, uranium, silver, lead, copper, iron, nickel and cobalt. This reagent gives a reddish-yellow or orange precipitate with mercuric and uranyl ions. From solutions of acetates, silver, lead, iron, nickel and cobalt also yield precipitates. Thallous salts form a very stable but soluble double salt with the reagent. Silver gives a red to yellow precipitate, according to the concentration of the solution. Lead gives a yellow precipitate from acetate solutions. Cupric ions in a buffered acetate solution give a green precipitate, while cuprous ions give an orange precipitate. Both mercuric and mercurous ions are quantitatively precipitated as a yellow-orange compound from acetate solutions. Ferrous ions yield a green precipitate in buffered acetate solutions, while nickel gives a yellow-green precipitate, and cobalt a brown precipitate under the same conditions. Uranyl ions are nearly quantitatively precipitated from acetate solutions, and the precipitate is clear yellow in color.

**Determination of uranium.** Hovorka and Sykora<sup>3,4</sup> have used isatin- $\beta$ -oxime for the determination of uranium.

**Procedure.** Heat to boiling a solution of a uranyl salt containing 0.002-0.3 g. of  $U_3O_8$  in 50-100 ml. of water. Add 5 to 60 ml. of a 1 per cent alcoholic solution of isatin- $\beta$ -oxime. Remove from the hot plate, and add 5-10 ml. of 10 per cent sodium acetate solution. An excess of both reagents is necessary, but the orange-yellow precipitate is not obtained from a uranyl nitrate solution except when buffered with sodium acetate. Allow to stand 2-3 hours, filter, wash with 20-100 ml. of water, and ignite and weigh as  $U_3O_8$ . The factor for uranium is 0.8480.

Results usually are a little high, but the error seldom exceeds 1 mg. of  $U_3O_8$ .

Attempts to weigh the precipitate of  $UO_2(C_8H_5N_2O_2)_2$  after drying at 105-110° C. have not been entirely successful, since the precipitate adsorbs some of the precipitant.

**Separation of uranium.** Uranium may be separated from nickel and cobalt, since at room temperatures the uranyl ion forms a precipitate with isatin- $\beta$ -oxime while nickel and cobalt ions do not.<sup>5</sup>

**Procedure.** To 20-80 ml. of a solution containing 0.002-0.1 g. of uranium and 0.05-0.3 g. of cobalt and/or 0.05-0.3 g. of nickel, add 10-15 ml. of a buffer prepared by making a 10 per cent sodium acetate solution acid to phenolphthalein, 5-15 ml. of a 2 per cent ammonium thiocyanate solution, 2.5-15 ml. of a 2 per cent sodium potassium tartrate solution, and 6-30 ml. of a 1 per cent isatin- $\beta$ -oxime solution in 50 per cent ethyl alcohol. Allow the solution to stand for 15 minutes, filter off the yellow uranyl isatoxime precipitate, and wash with about 100 ml. of 0.05 per cent isatin- $\beta$ -oxime solution. Ignite the precipitate and weigh as  $U_3O_8$ . The factor for uranium is 0.8480.

The errors obtained using this method ranged from +0.2-5 mg.

With a suitable modification of the above method, uranium can be separated from manganese, zinc, cobalt, strontium, barium and magnesium.<sup>6</sup>

**Procedure.** Heat to boiling 50-100 ml. of a solution containing 0.009-0.240 g. of the uranyl ion, as the nitrate, acetate, or chloride, and then add 6-60 ml. of a 1 per cent solution of isatin- $\beta$ -oxime in 50 per cent ethyl alcohol. Add 5-15 ml. of a cold 10 per cent solution of sodium acetate and allow the mixture to stand for three hours at room temperature. Filter, and wash the precipitate with hot water, or with a solution containing 25 ml. of reagent solution in 500 ml. of water, and ignite and weigh as  $U_3O_8$ .

This procedure gives results which are fairly accurate.

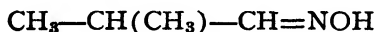
1. S. Gabriel, *Ber.* 16, 518 (1883).
2. V. Hovorka and V. Sykora, *Collection Czechoslov. Chem. Commun.* 10, 83-92 (1938); *C.A.* 32, 4460 (1938).
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## ISOBUTYRALDOXIME

$C_4H_9ON$

Mol. Wt. 147.16

Beil. Ref. 1-674(350).

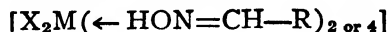


**Use:** Reaction with cobalt, copper and nickel.

Isobutyraldoxime is a colorless unpleasant smelling liquid. It boils at 139° C., and is moderately soluble in water.

**Preparation:** An aqueous solution of hydroxylamine hydrochloride is mixed with an equal quantity of sodium carbonate, and the cooled mixture is added to an alcoholic solution of isobutyraldehyde (a little more than theory). Allow the mixture to stand 12 hours, extract with ether, dry the ether extract with calcium chloride, and evaporate the ether on a water bath.<sup>1</sup>

**Reaction of cobalt, copper and nickel.** Cobalt chloride, nickel chloride, and cupric chloride react with four molecules of isobutyraldoxime by the direct crystallization of an alcohol solution of the reactants.<sup>2</sup> These compounds are non-electrolytes and have the following general formula

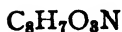


in which X is a halogen and M is a metal.

1. J. Petraczek, *Ber.* 15, 2784 (1882).
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**PHENYLGLYOXYLIC ACID OXIME**

Synonym: Isonitrosophenylacetic acid



Mol. Wt. 165.14

Beil. Ref. X, 655, 656(313).

**Use:** Detection of cobalt, copper, and nickel.

Phenylglyoxylic acid oxime exists in two isomeric forms, which are designated as the  $\alpha$ - and the  $\beta$ -compounds.

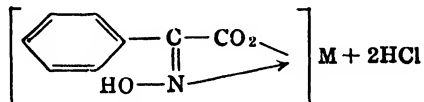
$\alpha$ -Phenylglyoxylic acid oxime is a crystalline solid melting at 127° C. with decomposition. It is easily soluble in water, alcohol and ether, but is only slightly soluble in chloroform and benzene.

$\beta$ -Phenylglyoxylic acid oxime consists of needles melting at 145° C. with decomposition. This compound is less soluble in water, ether and chloroform than the  $\alpha$ -isomer.

**Preparation:**  *$\alpha$ -Phenylglyoxylic acid oxime:* Mix phenylglyoxylic acid with hydroxylamine hydrochloride at 0° C. and allow the mixture to stand for 3-4 hours. The compound is obtained by extracting the mixture with ether and evaporating the ether in a vacuum.<sup>1</sup>

*$\beta$ -Phenylglyoxylic acid oxime:* The  $\beta$ -compound is obtained by treating phenylglyoxylic acid with hydroxylamine in an alkaline neutral or acid solution with warming or by allowing the mixture to stand for several days at ordinary temperature. The reagent is recovered by extracting the acidified solution with ether and evaporating the ether.<sup>2</sup>

**Reaction of phenylglyoxylic acid oxime with copper, nickel and cobalt.** Phenylglyoxylic acid oxime reacts with cobalt, copper or nickel chloride to form compounds having the following composition:

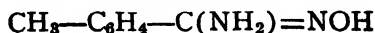


When the  $\alpha$ -compound is used in the presence of the metallic halides, it is quickly converted to the  $\beta$ -form, which then reacts to form the metal salt. The copper compound is bright green in color, while the cobalt compound is red.<sup>3</sup>

1. A. Hantzsch, *Ber.* 24, 42 (1891).2. A. Hantzsch, *Ber.* 24, 43 (1891).3. W. Hieber and F. Leutert, *Ber.* 62B, 1839-46 (1929); *C.A.* 23, 4692 (1929).**p-TOLUAMIDEOXIME**

Mol. Wt. 150.16

Beil. Ref. IX, 492.

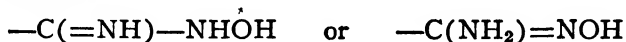
**Use:** Detection of copper and nickel.



*p*-Toluamideoxime is a crystalline solid melting at 145-146° C. It is soluble in alcohol, ether, chloroform and hot water. It is also soluble in acids and alkalies.

**Preparation.** Mix equivalent quantities of *p*-methylbenzonitrile, hydroxylamine hydrochloride, and sodium carbonate (crystalline), and dissolve in the least possible quantity of water. Carefully add alcohol until the solution is completely clear, and then heat in a closed vessel for six hours at 80-90° C. *p*-Toluamideoxime separates as a crystalline solid upon the evaporation of the alcohol. If sodium chloride precipitates, add a little water. The product is purified by recrystallizing two or three times from boiling water.<sup>1</sup>

**Detection of copper and nickel.** Werner<sup>2</sup> has observed that compounds containing the group



such as *p*-toluamideoxime form inner-complexes or normal salts of the type,  $-\text{C}(\text{NH}_2)=\text{NO}-\text{M}$ . The copper complex is brownish-green in color.

If an alcoholic solution of *p*-toluamideoxime is mixed with an aqueous or preferably an alcoholic solution of nickel chloride, air oxidation causes the development of an intense cherry-red color within a few days. The same results are obtained in a few seconds by adding hydrogen peroxide. This treatment yields, according to the concentration and the quantity of peroxide, a blue-violet, red, or red-violet color. The color is not stable and disappears in a few days on standing in air. The color may be due to an inner-complex salt of tetravalent nickel.<sup>3</sup> Malatesta and Pizzotti<sup>4</sup> claim that the complex is a salt of bivalent rather than tetravalent nickel.

1. L. H. Schubart, *Ber.* **19**, 1488 (1886).

2. A. Werner, *Ber.* **41**, 1069 (1908).

3. M. Kuras, *Chem. Obzor.* **16**, 72-4 (1941); *C.A.* **37**, 3367 (1943).

4. L. Malatesta and R. Pizzotti, *Gazz. chim. ital.* **72**, 564-7 (1942).

## CHAPTER XIII

### CUPFERRON AND NEOCUPFERRON

Since the nitroso substituted hydroxylamines exist in tautomeric equilibrium with the corresponding enol forms, compounds of this type may be classed as oximes. Only two members of this group have been used as analytical reagents, although they have been applied to many important procedures. These are cupferron (ammonium salt of N-nitroso-N-phenylhydroxylamine) and neocupferron (ammonium salt of N-nitroso-N-naphthylhydroxylamine).

#### CUPFERRON

Synonym: Ammonium salt of nitrosophenylhydroxylamine



Mol. Wt. 155.16

Beil, Ref. XVI, 669.



**Use:** Detection of barium, bismuth, cadmium, calcium, copper, iron, strontium, titanium, tungsten, uranium and vanadium.

Determination of aluminum, bismuth, columbium, copper, gallium, iridium, iron, mercury, molybdenum, tantalum, thorium, tin, titanium, uranium, vanadium and zirconium.

Cupferron is a white or buff colored crystalline powder. It melts at 163-164° C. It is freely soluble in water and in alcohol.

**Preparation:** *β-Phenylhydroxylamine:* Mix 250 g. of ammonium chloride and 8 liters of water with 416 ml. of nitrobenzene in a large earthenware jar. Equip with a mechanical stirrer, and while vigorously stirring shake in 620 g. of zinc dust during a period of 15-20 minutes, or rapidly enough to cause the temperature of the reaction mixture to rise to 60-65° C. Continue to stir for 15 minutes after all the zinc has been added, and then filter the reaction mixture through a large Buchner funnel using suction. Allow the filtrate to drain into a quantity of ice and salt mixture such that an excess of ice will remain when all the filtrate has been added. This provides for the rapid cooling and dilution of the filtrate. Allow the mixture to stand for a few minutes and filter the precipitated *β*-phenylhydroxylamine and wash with cold water. Use immediately for the preparation of cupferron.

*Cupferron:* Weigh the moist phenylhydroxylamine prepared as described above from 832 ml. of nitrobenzene (twice the quantity described above), and dissolve in 9 liters of ether. Filter and weigh the insoluble material to determine with fair accuracy the quantity of phenylhydroxylamine in the ether solution. Filter the ether solution through a dry filter paper into a 12-liter round bottom flask, and immerse the vessel in a cooling bath of water and ice. Equip

the flask with a mechanical stirrer and an inlet tube for ammonia gas and another for the introduction of butyl nitrite.

When the flask and contents are thoroughly cooled, pass ammonia gas through the mixture until an excess is present, and then add 95 g. of freshly distilled *n*-butyl nitrite for each 100 g. of phenylhydroxylamine present. Maintain a brisk flow of ammonia gas during the addition of the butyl nitrite. The latter is added slowly to prevent a rise in temperature. The addition period generally requires about one hour. Stir the solution for 10-15 minutes after the butyl nitrite has been added, and filter off the precipitate of cupferron and wash thoroughly with ether. Dry until free from ether by spreading in a thin layer on paper which is supported by large shallow metal trays. Store the compound in amber glass bottles. Suspend a small sack of ammonium carbonate from the stopper of the bottle to prevent decomposition.<sup>1-2</sup>

A method similar in all respects to that described above except that amyl nitrite is used in place of butyl nitrite has been proposed by Marvel and Kamm.<sup>3</sup> Slater<sup>4</sup> used methyl nitrite with essentially the same results.

Another procedure described by Kasonof<sup>5</sup> is based upon the conversion of nitrobenzene to phenylhydroxylamine by using ammonium chloride and amalgamated zinc dust. The reaction is carried out at a temperature below 16° C. for a period of one hour, and the phenylhydroxylamine is freed from zinc hydroxide and other insoluble matter by filtration, and is then salted out by means of sodium chloride. The phenylhydroxylamine is converted to cupferron by the method described by Marvel and Kamm.<sup>3</sup>

Slotta and Jacobi<sup>6</sup> described a method for the preparation of phenylhydroxylamine by the reduction of an alcoholic solution of nitrobenzene by using ammonia and hydrogen sulfide. They used 80 per cent alcohol which was saturated successively with ammonia and hydrogen sulfide to obtain a crystalline material which was treated with ether, filtered and washed with ether. The filtrate was composed of two layers, the upper one of which consisted of an ether solution of phenylhydroxylamine. These layers were separated and the ether layer saturated with ammonia gas, and cupferron then precipitated by the addition of gaseous ethyl nitrite.

**Cupferron as an analytical reagent.** The ammonium salt of nitroso-phenylhydroxylamine was first proposed as an analytical reagent by Baudisch<sup>7-17</sup> in 1909. The name cupferron, which is more convenient to use than the longer name, was proposed for this reagent, since it was observed to precipitate quantitatively both copper and iron. The name cupferron is misleading, however, since not only does the reagent precipitate copper and iron, but also many other elements such as vanadium, titanium, zirconium and tin. In addition to these common elements, cupferron also precipitates several other less familiar elements, such as gallium, columbium, tantalum and hafnium.

Cupferron is extremely useful as a reagent for the group separation of iron, titanium, vanadium and zirconium from aluminum, chromium and small quantities of phosphorus. In addition other valuable separations are: vanadium from hexavalent uranium; columbium and tantalum from aluminum, chromium and hexavalent uranium; and tin from copper, lead, trivalent arsenic and anti-

mony, after the precipitation of the last four elements from a hydrofluoric acid solution by means of hydrogen sulfide.

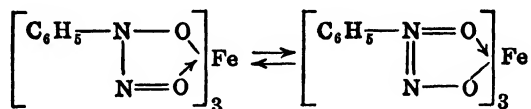
While the reagent is not as selective in its precipitating action as might be desired, it is nevertheless of great value in many analytical procedures. The more important of these are applied to the separation of those elements which are precipitated by cupferron from such metals as aluminum, chromium, manganese, nickel, cobalt, zinc and the alkaline earths with which they may be associated.

In addition to those procedures in which the elements precipitated by cupferron are later to be determined, many precipitations are carried out in which the elements are simply to be removed from the presence of other substances to prevent interference in their determination. As examples of this use, the preliminary precipitation of vanadium and iron with cupferron makes possible the determination of phosphorus in ferrocvanadium, or iron and copper may be removed before testing for cobalt with  $\alpha$ -nitroso- $\beta$ -naphthol.<sup>63</sup>

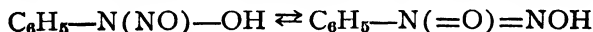
Virtually all the usual precipitations with cupferron are made in acid solutions. It is of interest to note that the selectivity of the precipitation reaction increases with the acidity; the most useful range is that of solutions containing from 5-10 per cent by volume of hydrochloric or sulfuric acid.

The fact that cupferron can be used for many precipitations in the presence of organic matter, such as tartaric and oxalic acids, further contributes to the usefulness of this reagent in analytical procedures.

Cupferron reacts with iron, copper, titanium, zirconium, vanadium, molybdenum, lanthanum, gallium and other metals to form inner-complexes, whose composition is represented by that of the iron compound. This substance may exist in two forms:



which correspond to the two tautomeric forms of nitrosophenylhydroxylamine.



These compounds are soluble in ether, although the copper complex dissolves only with some difficulty. The inner-complex character of the cupferron precipitates is indicated by the fact that an aqueous acetone solution of the iron compound is not affected by treatment with hydrogen sulfide. Further, no reaction is obtained when hydrogen sulfide is added to a suspension of the ferric salt in 2 N hydrochloric acid.

Solutions of cupferron are decomposed upon heating with the formation of nitrosobenzene. To prevent this, precipitations are always carried out in cold solutions, and better results are obtained if the solutions are cooled in ice. The precipitates should also be filtered as rapidly as possible after their formation, since the excess cupferron which is required for the precipitation is not particularly stable in acid solutions. Ammonium hydroxide and sodium carbonate are without appreciable action upon the precipitates, but the iron compound is

converted by sodium hydroxide to nitrosobenzene and this is accompanied by precipitation of ferric hydroxide.

Precipitates formed by the addition of cupferron to acid solutions of metallic salts cannot be weighed after drying, but must be ignited to the oxide and later weighed in this form. Macerated filter paper is added to the solution in which the precipitation is carried out to increase the bulkiness of the precipitate. This aids in the subsequent ignition of the precipitate, particularly if the precipitate is heated slowly with a gradual increase of the temperature.

**Solubility of the metallic derivatives of cupferron.** Pinkus and Martin<sup>18,19</sup> have studied the solubility of some of the derivatives of cupferron, and their results are listed in Table 65. No mention is made as to the effect of the excess precipitant upon the solubility of the various compounds, and this fact must be borne in mind in applying this information to the development of quantitative procedures.

As a result of these studies, Pinkus and Martin<sup>20</sup> have divided the metals into five groups based upon their solubility behavior:

I. Metals which are completely precipitated by cupferron, even in the presence of strong acids: mercurous, copper, bismuth, antimonous, tin and iron.

II. Metals which are almost completely precipitated in a neutral solution but are not precipitated in an acid solution: Aluminum.

III. Metals which are partially precipitated in a neutral or weakly acetic acid solution, but which are not precipitated in presence of strong acids: lead, cadmium, nickel, and cobalt (these metals are almost completely precipitated, particularly lead and cadmium, by precipitating rapidly and with a large excess of cupferron).

IV. Metals which are partially precipitated in a neutral solution but which are not precipitated in an acid solution: silver, mercuric, chromium, manganese and zinc.

V. Metals which are not precipitated even in neutral concentrated solutions: trivalent and pentavalent arsenic and pentavalent antimony.

Lundell and Hoffman<sup>21</sup> have studied the precipitation of various elements by cupferron in solutions which are made 3.5-4.5 N in sulfuric or hydrochloric acids. The elements which are completely precipitated under these conditions are titanium, vanadium, zirconium, columbium, molybdenum, hafnium, tantalum, tungsten, iron, palladium, gallium, tin, antimony, bismuth and polonium. Elements which are partially precipitated include copper, thallium, thorium, proto-actinium, actinium, lanthanum and other metals of the rare earth group. In addition, uranium, nitrogen, phosphorus and silicon may interfere under certain conditions.

It will be observed from the above studies that if all the elements precipitated by cupferron were likely to occur in most substances which are commonly submitted for analysis, the reagent would be of little value. Many of the elements, however, such as zirconium, columbium, molybdenum, tungsten, uranium, lanthanum and the rare earths are not commonly found in many materials, and so the usefulness of the reagent as a precipitant is greatly increased. In the analysis

TABLE 65.—THE SOLUBILITY OF THE METAL COMPOUNDS OF CUPFERRON

Cation	Precipitation Medium	Coagulation of	Color of Precipitate	H <sub>2</sub> O Solubility at 18° C. mg./liter	Solubility in N HCl at 18° C. gm. at./l.	Solubility in N Acetic Acid at 18° C. gm. at./l.	Action of N KOH at 18° C.	Action of N NH <sub>4</sub> OH at 18° C.
Fe <sup>++</sup>	Neutral and Acid	Easy <sup>1</sup>	Brown <sup>1</sup>	0.02	$2 \times 10^{-4}$	Very feeble	Feeble decomp.	$4 \times 10^{-4}$ <sup>2</sup>
Fe <sup>++</sup>	Neutral and Acid	Easy <sup>1</sup>	Brown <sup>1</sup>	0.02	$2 \times 10^{-4}$	Very feeble	Feeble decomp.	$4 \times 10^{-4}$ <sup>2</sup>
Hg <sup>+</sup>	Acid	Easy <sup>1</sup>	White	0.3	Very feeble	Very feeble	Attacked	Attacked
Cu <sup>++</sup>	Acid	Easy <sup>1</sup>	Gray-blue	0.7	$5 \times 10^{-4}$	Very feeble	Feeble decomp.	Dissolved
Sn <sup>+++</sup>	Acid	Difficult <sup>2</sup>	White	2.4	$10^{-4}$	Very feeble	Dissolved	Attacked <sup>3</sup>
Al <sup>+++</sup>	Acid <sup>1</sup>	Easy <sup>1</sup>	White	0.9	$10^{-3.6}$	Feeble	Feeble decomp.	Feeble attack
Sn <sup>++</sup>	Neutral and Acid	Difficult <sup>2</sup>	White	4.2	$10^{-4}$	Very feeble	Dissolved	Attacked <sup>3</sup>
Bi <sup>+++</sup>	Neutral and Acid	Easy <sup>1</sup>	White	8.4	$6 \times 10^{-4}$	Very feeble	Very feeble	$10^{-4}$
Pb <sup>++</sup>	Neutral and Acid	Difficult <sup>2</sup>	Yellowish	5.5	$10^{-4}$	Very feeble	Dissolved	Attacked <sup>3</sup>
Pb <sup>++</sup>	Neutral and HAc	Easy <sup>1</sup>	White	25.0	Notable	$2 \times 10^{-3}$	Dissolved	Attacked
Pb <sup>++</sup>	Neutral and HAc	Easy <sup>1</sup>	White	40.0	Notable	Sensible	Attacked	Dissolved
Cd <sup>++</sup>	Neutral and HAc	Difficult <sup>2</sup>	White	32.0	Notable <sup>7</sup>	Notable <sup>7</sup>	Dissolved <sup>7</sup>	Dissolved <sup>7</sup>
Zn <sup>++</sup>	Neutral and HAc	Easy <sup>1</sup>	Greenish-white	52.0	Notable	Sensible	Attacked	Dissolved
Ni <sup>++</sup>	Neutral and HAc	Easy <sup>1</sup>	Reddish-brown <sup>5</sup>	77.0	Notable	Sensible	Attacked	Dissolved
Co <sup>++</sup>	Neutral and HAc	Easy <sup>1</sup>	White	150.0	Notable	Notable	Attacked	Dissolved
Ag <sup>+</sup>	Neutral	Difficult	Yellowish	Notable	Notable	Notable	Attacked	Attacked
Hg <sup>++</sup>	Neutral	Difficult <sup>1</sup>	Green	Notable	Notable	Notable	Attacked	Attacked
Cr <sup>+++</sup>	Neutral	Easy	Rose	Notable	Notable	Notable	Attacked	Attacked
Mn <sup>++</sup>	Neutral	Easy		Notable	Notable	Notable	Attacked	Attacked

<sup>1</sup> Also when very feebly acid.<sup>2</sup> In sufficiently concentrated solution. In dilute solution the supernatant liquid is cloudy.<sup>3</sup> Upon agitation with excess cupferron, a resinous mass is obtained.<sup>4</sup> The ferrous salt gives a blood-red precipitate, which rapidly transforms to the ferric-brown color.<sup>5</sup> Brown salt in the presence of acetic acid.<sup>6</sup> After filtration and washing the fresh precipitate re-dissolves easily in acid.<sup>7</sup> Before transformation into a resinous mass which resists action of acids and bases.<sup>8</sup> Formation of colloidal solutions.

of the ferrous metals and alloys, the non-ferrous elements such as tin, antimony and bismuth are rarely present; and similarly in the analysis of many non-ferrous materials iron may not be present. In many cases interfering elements can be removed by a preliminary separation by means of hydrogen sulfide or other reagents. A mixed precipitate of the iron and copper complexes can be separated into a pure precipitate of the iron derivative and a filtrate containing the copper salt by washing the mixed precipitate with a solution of ammonium hydroxide. Thus it will be seen that cupferron does possess advantages which might not at first sight be apparent in the light of its lack of specificity as a precipitant.

Auger and co-workers<sup>22</sup> have prepared and studied a number of compounds of cupferron with various metals. The compounds formed are listed in Table 66.

TABLE 66.—DERIVATIVES OF CUPFERRON  
[C = C<sub>6</sub>H<sub>6</sub>N(NO)O]

Metal	Formula	Description	Medium
Silver	AgC		Neutral
Lead	PbC <sub>2</sub>	White	Neutral or faintly acid
Mercury	Hg <sub>2</sub> C <sub>2</sub>		Acid
Mercury	HgC <sub>2</sub>	White	Slightly acid
Bismuth	BiC <sub>2</sub>	White	Acid
Cadmium	CdC <sub>2</sub>		Neutral or acetic acid
Stannous	SnC <sub>2</sub>	White	
Stannic	SnC <sub>4</sub>	White	
Antimony	SbC <sub>3</sub>		Neutral
Molybdenum	CMoO <sub>3</sub> C <sub>2</sub> MoO <sub>3</sub>	Obtained together by adding cupferron to hydrochloric acid solution containing MoO <sub>3</sub> .	
Cerous	CeC <sub>3</sub>	Yellow	Neutral
Ceric	CeC <sub>4</sub>	Rusty	Neutral
Chromium	CrC <sub>3</sub>	Green	Neutral
Indium	InC <sub>3</sub>	White	Acid
Cobalt	CoC <sub>3</sub>	Pink	Neutral
Nickel	NiC <sub>3</sub>	Green	Neutral
Zinc	ZnC <sub>2</sub>		Neutral
Barium	BaC <sub>2</sub> ·3H <sub>2</sub> O	White	Neutral
Strontium	SrC <sub>2</sub> ·2H <sub>2</sub> O		Slightly soluble in hot water
Calcium	CaC <sub>2</sub> ·2H <sub>2</sub> O		Slightly soluble in hot water

**Stability of aqueous solutions of cupferron.** Cupferron dissolves readily in water, but the resulting solution decomposes somewhat on long standing. Germuth<sup>23</sup> has suggested that the stability of aqueous solutions of cupferron can be improved by adding 50 mg. of acetophenetide to each 150 ml. of the reagent solution. He reports that such solutions do not undergo any appreciable change within 20 days, and that at ordinary temperatures and upon exposure to daylight the decomposition is not apparent until after 30 days. Baudisch<sup>10</sup> states that the reagent can be kept indefinitely by simply suspending a lump of ammonium carbonate in the container in which the reagent is stored. Decomposition of the reagent solution may be detected by the turbid appearance of such

solution and the formation of brown decomposition products. Baudisch<sup>10</sup> also claims that an ammoniacal solution of the reagent will keep for at least one month.

**Determination of copper.** Baudisch<sup>7-9,17</sup> originally proposed the use of cupferron as a precipitant for both copper and iron. This reaction was later studied by Biltz and Hodtke,<sup>24</sup> who found that copper is completely precipitated from weak solutions of hydrochloric acid containing sodium acetate, but that precipitation is not complete in the presence of large quantities of the mineral acids. Hanus and Soukup<sup>25</sup> experienced considerable difficulty in precipitating copper from dilute sulfuric acid solutions, but obtained satisfactory results by using a large excess of the reagent, and immediately filtering after precipitation. The determination is carried out by igniting the precipitate to the oxide, and then reducing with methyl alcohol. Fresenius<sup>26</sup> has shown that copper is quantitatively precipitated from acetic acid solutions containing ammonium acetate. The precipitate is washed free of excess reagent with 1 per cent sodium carbonate solution, ignited completely and then ignited with sulfur in an atmosphere of hydrogen to form  $\text{Cu}_2\text{S}$ . Webber<sup>27</sup> has also studied the precipitation of copper with cupferron. More recently Benedetti<sup>28</sup> has used cupferron for the determination of iron and copper in the analysis of clay, and Surenov<sup>29</sup> has applied the reagent to the determination of iron and copper in chrome-plating baths.

Copper is not quantitatively precipitated in the presence of high concentrations of mineral acids, although very dilute solutions of hydrochloric or sulfuric acids are not objectionable. Best results are obtained by precipitating copper from an acetic acid solution in the presence of sodium or ammonium acetate, but under these conditions the precipitation is far less specific. Cold water is most satisfactory as a wash liquid. The precipitate is usually ignited to the oxide, although the copper may be converted to cuprous sulfide by igniting with sulfur in the presence of hydrogen, or it may be reduced to the metal.

Biltz and Hodtke<sup>24</sup> reported that lead, mercury, silver and tin interfere with the copper determination, and Fresenius<sup>26</sup> later added bismuth to this list. In addition, iron, titanium, zirconium, cerium, thorium, tungsten, vanadium and probably other elements also interfere. Interference by iron, titanium, zirconium, cerium, and thorium and possibly also lead, mercury, tin, and bismuth can be avoided by treating the copper precipitate with ammonium hydroxide and reprecipitating the dissolved copper with dilute acid. Despite the fact that excellent results are obtained by precipitating copper from pure solutions of its salts with cupferron, this reagent seems to offer few if any advantages over other well-known methods for the determination of copper.<sup>30</sup>

**Separation of copper with cupferron.** *Copper from zinc:* Copper may be precipitated from a slightly acid solution containing copper and zinc salts. Most satisfactory results are obtained in presence of acetic acid.<sup>24</sup> Hanus and Soukup<sup>25</sup> have attempted this separation in the presence of sulfuric acid, but report that their results were not entirely satisfactory. Rothschild<sup>31</sup> has used cupferron for the determination of copper as an impurity in zinc.



**Copper from cadmium:** Biltz and Hodtke<sup>24</sup> report a good separation of copper from cadmium in dilute solutions of hydrochloric acid, but report that results were not satisfactory in acetic acid solutions. Hanus and Soukup<sup>25</sup> attempted the separation in a 5-10 per cent sulfuric acid solution.

**Copper from iron:** Baudisch<sup>7</sup> and Biltz and Hodtke<sup>24</sup> have found that a good separation of copper and iron can be effected by precipitating these two metals with cupferron from a weakly acid solution, and then washing the precipitate on the filter with ammonium hydroxide solution. The copper precipitate is dissolved with this treatment, but the iron compound remains insoluble. Fresenius<sup>26</sup> reports excellent results in separating copper and iron by precipitating these metals with cupferron in an acetic acid solution containing ammonium acetate, and then washing the precipitate with ammonium hydroxide.

**Copper from selenium:** Angeletti<sup>32</sup> has obtained a quantitative separation of selenium by precipitating copper with cupferron in the usual manner. An excess of the reagent must be avoided. This is an important separation, since selenium is usually determined by reducing with sulfur dioxide, and if the copper is not previously removed it is also reduced by this treatment.

**Detection of copper.** Copper may be detected by means of the crystalline precipitate which it yields with cupferron. A microscopic procedure is recommended. Cadmium, uranium, barium, calcium, strontium and iron give similar reactions.<sup>186,187</sup>

**Determination of iron.** Iron, like copper, is quantitatively precipitated in an acid solution upon the addition of cupferron. This reaction has been used by Baudisch and others for the determination and separation of iron.<sup>7-9,11,12,17,84,188</sup>

Iron is best precipitated from dilute solutions of mineral acids and from acetic acid solutions. Complete precipitation has been obtained from solutions containing as high as 20 per cent by volume of sulfuric acid. The precipitate may be washed with cold 2 N hydrochloric acid, ammonium hydroxide or with water. The usual method of determination is based upon the ignition of the precipitates to  $\text{Fe}_2\text{O}_3$  and weighing in that form.<sup>85</sup>

The following method for the determination of iron in presence of cobalt, nickel, zinc, chromium, aluminum and manganese is taken from the work of Fresenius:<sup>26</sup>

**Procedure.** Make the solution containing the ferric salt slightly acid with hydrochloric, sulfuric, nitric, acetic or perchloric acid, and add to the cold solution an excess of a 6 per cent aqueous solution of cupferron with constant stirring. The hydrochloric acid concentration corresponds to 20 ml. of concentrated hydrochloric acid per 150 ml. of solution. The brown precipitate of the cupferron compound forms and quickly coagulates. An excess of the reagent is indicated by the formation of a white precipitate of nitrosophenylhydroxylamine. The formation of this compound occurs when the precipitations are carried out in solutions containing mineral acids, but not in solutions which have been acidified with acetic acid. Allow the mixture to stand for 15 minutes

in the cold, and filter the precipitate through an ashless filter paper, using a filter cone and slight suction. The filtrate should be clear and colorless except when nickel, cobalt or chromium salts are present. Wash the precipitate with water, and then with a little dilute ammonium hydroxide to remove any excess of the precipitant. Finally wash with water to remove ammonia, and then transfer the filter paper and contents to a weighed platinum crucible. Dry, and ignite gently to decompose the organic matter. Finally ignite at a bright red heat to constant weight, and weigh as  $\text{Fe}_2\text{O}_3$ .

Fresenius<sup>26</sup> has studied the precipitation of iron with cupferron under various conditions of acidity and in the presence of various ions, and the results of his work are shown in Table 67.

TABLE 67.—THE DETERMINATION OF IRON IN THE PRESENCE OF VARIOUS IONS AND IN DIFFERENT MEDIA

Fe Taken g.	Fe Found g.	Diff. mg.	Elements Other than Fe Present	Vol. Sol. ml.	Remarks
0.0884	0.0887	+0.3	.....	150	HCl, 20 ml. dil. acid excess
0.0593	0.0594	+0.1	.....	150	$\text{H}_2\text{SO}_4$ , 20 ml. dil. acid excess
0.1295	0.1302	+0.7	.....	150	$\text{HNO}_3$ , 20 ml. dil. acid excess
0.0737	0.0738	+0.1	.....	150	$\text{HC}_2\text{H}_3\text{O}_2$ , 20 ml. dil. acid excess
0.0260	0.0255	—0.5	0.0734 g. Al	150	HCl soln., Al as $\text{AlCl}_3$
0.0731	0.0729	—0.2	0.0986 g. Al	150	HCl soln.
0.0383	0.0387	+0.4	0.0509 g. Al	150	HCl soln.
0.0491	0.0493	+0.2	5 g. $\text{NH}_4\text{Cl}$	150	HCl soln.
0.0600	0.0605	+0.5	5 g. $\text{K}_2\text{SO}_4$	200	$\text{H}_2\text{SO}_4$ soln.
0.0258	0.0261	+0.3	2 g. $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	150	HCl soln.
0.0362	0.0365	+0.3	About 2 g. $\text{CaCl}_2$	150	2 g. $\text{CaCO}_3$ dissolved in excess HCl
0.0652	0.0652	0.0	2 g. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	150	HCl soln.
0.0376	0.0375	—0.1	About 2 g. $\text{CrCl}_3$	150	1 g. $\text{Cr}_2\text{O}_3$ dissolved in excess dil. HCl
0.0457	0.0455	—0.2	1 g. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	150	$\text{H}_2\text{SO}_4$ soln.
0.0416	0.0414	—0.2	1 g. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	150	$\text{H}_2\text{SO}_4$ soln.
0.0288	0.0292	+0.4	2 g. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	150	$\text{H}_2\text{SO}_4$ soln.

Ferrari<sup>36</sup> has used cupferron for the rapid determination of iron in the presence of soluble organic substances, and he has shown that quantitative determinations of iron can be made in the presence of these materials in about one and one-half hours by direct precipitation with cupferron of chlorine-treated, hydrochloric acid solutions of organic materials, followed by filtration of the precipitate and ignition to  $\text{Fe}_2\text{O}_3$ . Copper, silver, lead, mercury, tin, bismuth, titanium and zirconium, however, are reported to interfere with this procedure.

Lehrman and co-workers<sup>37</sup> have used cupferron for the determination of iron after its separation from interfering substances by means of hexamethylene-tetramine.

Gapchenko<sup>38</sup> has used cupferron in a titrimetric method for the indirect determination of iron. Iron is precipitated with cupferron in the usual manner, the precipitate is dissolved in acetone, and an aliquot part of this solution is titrated with a solution of trivalent molybdenum. The nitroso group is reduced by the molybdenum to an amino compound, and this step is followed by the titration of the excess trivalent molybdenum with ferric ammonium alum in the presence of methylene blue as an indicator.

Many special methods have been proposed for the determination of iron in special materials, such as clay<sup>28</sup> and silicate minerals.<sup>39</sup> Schroeder<sup>40</sup> has also used cupferron for the determination of iron in ferrocyanides to determine the purity of the material. Most of these special methods involve the determination of iron in the presence of other ions, and the discussion of these procedures will be considered in the following section on the separation of iron by means of cupferron.

**Separation of iron. Iron from copper:** Both copper and iron are precipitated when cupferron is added to an acid solution containing these cations, but iron and copper may be separated by treating the mixture of the cupferron compounds with ammonium hydroxide. The copper salt dissolves, while the iron compound remains insoluble. By this method a complete separation of iron and copper is possible.<sup>24,26</sup> Matveev<sup>41</sup> has applied cupferron to the analysis of pyrite containing copper.

**Iron from manganese:** Cupferron provides an excellent means of determining iron in the presence of manganese. Fresenius<sup>26</sup> reports that iron in manganese ores and ferromanganese can be precipitated and washed free of manganese in a single precipitation, and this has been confirmed by other investigators.<sup>26,42-45</sup>

The following method may be used for the determination of iron in manganese ores:<sup>26</sup>

**Procedure.** Dissolve about 1 g. of finely pulverized ore in concentrated hydrochloric acid and evaporate the solution to dryness. Moisten the residue with a little concentrated hydrochloric acid, dilute with water, and heat to boiling. Filter, and fuse the residue with sodium carbonate in a covered platinum crucible. Dissolve the melt in water and dilute hydrochloric acid, and evaporate this solution to dryness. Remove silica in the usual manner, and add the filtrate to the main solution. Add 50 ml. of 6 per cent cupferron solution in a small stream by allowing to flow down the sides of the beaker while stirring vigorously. Continue the addition of the reagent solution until a drop of the reagent causes the formation of a white precipitate of nitrosophenylhydroxylamine. Add a slight excess of the reagent, and allow the mixture to stand for about 10 minutes, and then filter through an ashless paper with gentle suction. Complete the transfer of the last few particles of the precipitate which adhere to the beaker by adding a little ether to the beaker, and then remove the ether by adding a

little boiling water. Wash the precipitate with cold water until the filtrate is no longer acid to litmus. Then wash with 6 N ammonium hydroxide to remove the excess reagent and convert the iron compound to ferric hydroxide. Finally, wash the filter with cold water and ignite the precipitate to  $\text{Fe}_2\text{O}_3$ .

The results obtained in three analyses of manganese ores are given in Table 68.

TABLE 68.—THE DETERMINATION OF IRON-PYROLUSITE ( $\text{MnO}_2$ ) USING CUPFERRON

Sample No.	Iron Titrimetric Determination per cent	Iron Cupferron Method per cent	Diff. per cent	Remarks
1	18.25	18.23	-0.02	$\text{Fe}_2\text{O}_3$ was Mn free
2	18.49	18.56	+0.07	$\text{Fe}_2\text{O}_3$ was Mn free
3	17.93	18.03	+0.10	$\text{Fe}_2\text{O}_3$ was Mn free

Cunningham and Price have used cupferron for determining iron in manganese steel.<sup>46</sup>

**Iron from zinc:** Fresenius<sup>26</sup> reports that separation of iron from zinc is complete when the iron is precipitated with cupferron from a dilute sulfuric acid solution. Rothschild<sup>81</sup> has used this fact in determining copper as an impurity in zinc.

**Separation from aluminum and chromium.** Biltz and Hodtke<sup>24</sup> have used cupferron for the separation of iron from aluminum and chromium. Iron is precipitated in a mineral acid solution, and the precipitate washed with 2 N hydrochloric acid, water, ammonium hydroxide, and finally with water before igniting to ferric oxide. Fresenius<sup>26</sup> has shown that this separation is complete in a dilute hydrochloric acid solution. A similar procedure has also been used by Brown<sup>45</sup> for the precipitation of iron, titanium and zirconium from solutions containing these elements mixed with aluminum and manganese. Many important separations and determinations have been based upon this reaction. Belasio<sup>47</sup> has used the cupferron precipitation for the determination of iron in commercial aluminum and its light alloys. Lundell and Hoffman<sup>48</sup> have described a method for the determination of aluminum in bauxite and refractories of high aluminum content. In this method the sample is dissolved with the aid of sulfuric, nitric and hydrofluoric acids, and the solution is then evaporated to remove silica and hydrofluoric acid. The sample is then dissolved and the resulting solution divided into three aliquot portions. In one portion  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{P}_2\text{O}_5$  and  $\text{V}_2\text{O}_5$  are precipitated with ammonium hydroxide. In the second portion  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{V}_2\text{O}_5$  are precipitated with cupferron. The  $\text{P}_2\text{O}_5$  is determined in the third portion by means of the usual procedure, and  $\text{Al}_2\text{O}_3$  is found by difference.

Cunningham<sup>49</sup> has published a method for the determination of aluminum in

ferrochromium and chromium metal. Cupferron is used in this method to separate iron and aluminum. Chromium is oxidized by evaporating the solution with perchloric acid, and aluminum is determined by precipitation with ammonium hydroxide. The following procedure is taken from the published method of Cunningham:<sup>49</sup>

**Procedure.** Transfer 2.5 g. of the sample to a 250-ml. covered beaker, and treat with 15 ml. of hydrochloric acid (d. 1.19). If the aluminum content is less than 0.1 per cent, use a 10-g. sample. To do this, dissolve four 2.5-g. portions of the sample, and later combine the four aluminum hydroxide precipitates, obtained as described below, by filtering on a single 9-cm. paper and washing with a 2 per cent ammonium chloride solution. Warm the solution to about 60° C. until all action has ceased, and add 3 ml. of 30 per cent hydrogen peroxide. Evaporate the liquid to a syrup, and add 30 ml. of 1:1 hydrochloric acid. Heat the solution until all salts are dissolved, dilute with water to 50 ml., and filter on a 9-cm. paper containing ashless paper pulp into a 400-ml. beaker. Wash the paper and residue 18-20 times with hot water and ignite in a 30-ml. platinum crucible. Add 5 drops of 1:1 sulfuric acid and 2 ml. of 48 per cent hydrofluoric acid, and then volatilize the silica by evaporating the solution until the acids are completely expelled.

Fuse the residue with 2 g. of sodium carbonate, and dissolve the melt in 25 ml. of hot 1:4 sulfuric acid. If four 2.5-g. portions were used in the analysis, combine the residues and make only one fusion, using 8 g. of sodium carbonate. Boil the solution to expel carbon dioxide, and add approximately 2 g. of ammonium chloride and a very slight excess of filtered 1:3 ammonium hydroxide. Boil the solution for not longer than 1-2 minutes. Filter the precipitate on a 9-cm. paper containing some ashless paper pulp, and wash thoroughly with hot 2 per cent ammonium chloride solution. Transfer the paper containing the precipitate to the 400-ml. beaker containing the main solution, and macerate to a pulp by means of a glass rod. Heat the liquid almost to boiling for about 5 minutes to ensure complete solution of the precipitate.

Cool the solution, which should have a volume of about 100 ml. and an acidity of approximately 15 per cent, to 15° C. and precipitate iron by the addition of a slight excess of a freshly prepared, cold, 6 per cent solution of cupferron. All aluminum and chromium remain in the solution. A brownish-red, partly amorphous, partly crystalline precipitate separates. As soon as a drop of the reagent causes the formation of a transient, snow-white, crystalline precipitate, all iron is precipitated. Filter the precipitate on an 11-cm. paper containing some ashless paper pulp. Wash the paper and precipitate well with cold 5 per cent hydrochloric acid, and discard.

Collect the filtrate and washings in a 600-ml. beaker, and evaporate to a volume of about 50 ml. Add 50 ml. of nitric acid (d. 1.42), and continue boiling until the volume is reduced to approximately 10 ml. Add 20 ml. of nitric acid (d. 1.42) and 30 ml. of 60 per cent perchloric acid, and evaporate the solution to strong fumes of perchloric acid. Heat for an additional 30 minutes to ensure complete oxidation of chromium to chromic acid. Add 100 ml. of water, warm the solution, filter on a 9-cm. paper, and wash with warm water.

Collect the filtrate and washings, which should have a volume not exceeding 175 ml., in a 400-ml. beaker.

Nearly neutralize the solution with filtered 1:3 ammonium hydroxide, and heat to boiling. Add approximately 5 g. of ammonium chloride and some ashless paper pulp, and then add dropwise 1:3 ammonium hydroxide until the color just changes to a distinct yellow of the chromite. Boil the solution for not longer than 1-2 minutes, and immediately filter on a 9-cm. paper. Wash the paper and precipitate thoroughly with a hot 2 per cent ammonium chloride solution, transfer to a 150-ml. beaker, and treat with 15 ml. of 1:2 hydrochloric acid. Heat the solution to boiling for several minutes, dilute with warm water to 100 ml., and treat with a brisk stream of hydrogen sulfide for 15 minutes to precipitate platinum. Filter any precipitate that forms on a 9-cm. paper, wash 10-12 times with an aqueous solution of hydrogen sulfide containing 1 per cent hydrochloric acid, and discard.

Boil the filtrate to expel hydrogen sulfide, add 5 ml. of 60 per cent perchloric acid, and evaporate the solution to strong fumes of perchloric acid. Heat for an additional 15 minutes. Add 100 ml. of warm water, and nearly neutralize the solution with filtered 1:3 ammonium hydroxide, and then heat to boiling. Add approximately 2 g. of ammonium chloride, some ashless paper pulp, and several drops of a 0.2 per cent alcoholic solution of methyl red, and then add dropwise filtered 1:3 ammonium hydroxide until the color just changes to a distinct yellow. Boil the solution for not longer than 1-2 minutes, and filter immediately on a 9-cm. paper. Wash the paper and precipitate thoroughly with a hot 2 per cent ammonium chloride solution.

Ignite the precipitate in a weighed platinum crucible, first at a low temperature, and finally over a blast lamp for 5 minutes, or in an electric furnace at 1150° C. for 15 minutes. Cover the crucible with a closely fitting lid, and allow to stand in a desiccator until cool, and then weigh rapidly. A second heating of equal duration is advisable, especially as it permits more rapid weighing and consequently more accurate results. Ignited alumina is very hygroscopic and absorbs within the first 10 minutes' exposure to the air a large proportion of the total water which it will take up in 24 hours. A close-fitting crucible cover is quite efficient in preventing the adsorption of moisture by the alumina while the crucible is in the desiccator or on the balance pan.

The precipitate obtained as described contains part or all of the phosphorus in the alloy (depending upon the aluminum content), but rarely contains chromium; should it be colored, indicating the presence of chromium sesquioxide, treat as follows:

**Procedure.** Fuse with 1-2 g. of sodium carbonate. Dissolve the melt in the smallest possible quantity of hot water, and determine chromium colorimetrically. Add a small amount of sodium peroxide, and boil the liquid for a few minutes and cool. Transfer the chromate solution to a Camp comparison tube. The volume should now be about 15 ml. To the other comparison tube, add from a 10-ml. buret an amount of standard potassium chromate solution (1 ml. = 0.00050 g. Cr) which contains slightly less chromium than the sample, and sufficient water to make their volumes exactly equal. Mix well

and compare the intensity of the two solutions. The color of the sample should be slightly more intense than that of the standard. Add an additional small amount of the standard chromate solution to the tube containing the standard, and an equal amount of water to the tube containing the sample. Mix the contents of the tubes and again compare the intensities of the colors. Repeat these operations until the colors match exactly. The weight of chromium sesquioxide to be deducted is found by multiplying the number of ml. of the chromate solution used by 0.00050 and 1.4615.

After determining chromium colorimetrically, transfer the solution from the sodium carbonate fusion to a 300-ml. Erlenmeyer flask, and make acid with an excess of 2 ml. of nitric acid (d. 1.42). Heat the solution to boiling to expel carbon dioxide, and reduce the chromium to the trivalent state by the addition of sulfurous acid, followed by boiling. Cool the liquid to 40° C. and add approximately 5 g. of ammonium nitrate; 0.05 g. of ferrous sulfate (phosphorus-free), and 40 ml. of molybdate solution, and precipitate phosphorus as ammonium phosphomolybdate by shaking vigorously for 5 minutes. Allow the precipitate to settle, and determine phosphorus either by the alkalimetric or the molybdenum reduction (Emmertson) method. The weight of the phosphorus found multiplied by 2.2887 is the weight of phosphorus pentoxide to be deducted from the weight of the alumina precipitate.

The weight of the alumina precipitate, less the weight of chromic oxide and phosphorus pentoxide found, is multiplied by 52.94 and divided by the weight of sample taken to give the percentage of aluminum in the alloy.

A blank should be run on all the reagents used and any aluminum found deducted from the result obtained as described above. The results obtained using this method are shown in Table 69.

TABLE 69.—SEPARATION OF IRON AND ALUMINUM

Experiment No.	Ferro-Chromium Taken g.	Aluminum Added g.	Aluminum Found g.	Aluminum Recovered <sup>1</sup> g.	Error g.
1	5	Nil	0.00105		
2	5	Nil	0.00100		
3	10	Nil	0.00220		
			Av. 0.021%		
4	5	0.00228	0.00339	0.00234	+0.00006
5	5	0.0039	0.00498	0.00393	+0.00003

<sup>1</sup> After correcting for 0.021 per cent Al in alloy.

Among the special determinations in which cupferron is employed to separate iron from aluminum or chromium are the following: determination of aluminum in nickel-chromium and nickel-chromium-iron alloys;<sup>50</sup> the separation of iron and aluminum in the analysis of silicate and aluminate minerals;<sup>51</sup> separation of iron in the analysis of nickel-aluminum-iron alloys;<sup>52</sup> separation of iron as a step in the determination of aluminum in tungsten;<sup>53</sup> the deter-

mination of iron in chrome-plating baths;<sup>29</sup> and the removal of iron as a preliminary to the determination of aluminum in steel.<sup>151</sup>

In a recent study of the atomic weight of aluminum, Hoffman and Lundell<sup>54</sup> checked the purity of the aluminum used by means of chemical and spectroscopic procedures. According to this investigation iron, vanadium, titanium, zirconium, tin and gallium are completely precipitated by cupferron in a solution containing 5 ml. of sulfuric acid in 100 ml. of solution. A double precipitation of iron by cupferron, beginning with a 21 g. sample of very pure aluminum, revealed a 0.003 per cent iron content. Qualitative tests indicated that the  $\text{Fe}_2\text{O}_3$  obtained in the cupferron procedure was free of copper, although the aluminum was originally found to contain 0.002 per cent of this element.

**Iron from nickel and cobalt.** Baudisch first showed that iron can be satisfactorily separated from nickel and cobalt by precipitation with cupferron in a hydrochloric acid solution. Biltz and Hodtke<sup>24</sup> and Fresenius<sup>26</sup> also reported a good separation of these metals in solutions of mineral acid.

Nissenson<sup>55</sup> has used cupferron for the precipitation of iron as a preliminary to the determination of nickel and cobalt in arsenical sulfide ores.

**Procedure.** Dissolve 1 g. of the ore in 20 ml. of a saturated solution of bromine in concentrated hydrochloric acid, and evaporate the solution somewhat to remove volatile arsenious chloride. Add 10 ml. of 18 N sulfuric acid and evaporate the solution until dense fumes of sulfur trioxide appear. Then dilute to 500 ml., heat to boiling, and treat with hydrogen sulfide to precipitate the metals of the copper group, and any arsenic which may remain in the solution. Filter and heat the filtrate to expel hydrogen sulfide. Oxidize with hydrogen peroxide or ammonium persulfate, and then add slowly a solution of 8 g. of cupferron in 100 ml. of water to precipitate iron. Again filter and determine iron in the precipitate. Determine nickel and cobalt electrolytically in the filtrate after evaporating until fumes of sulfur trioxide are evolved.

Hoffman<sup>56</sup> has described a method for the determination of cobalt in magnet and high-speed tool steels in which iron and copper are removed by precipitation with cupferron. The greater part of the iron is removed by a preliminary extraction with ether, and chromium and vanadium are eliminated by precipitating with sodium hydroxide and peroxide. The iron still remaining after the ether extraction, together with any copper which may be present, is precipitated by cupferron in a dilute hydrochloric acid solution, and the cobalt is then precipitated in the filtrate with  $\alpha$ -nitroso- $\beta$ -naphthol. Cupferron does not interfere in the precipitation of cobalt by  $\alpha$ -nitroso- $\beta$ -naphthol.

**Iron from the alkali and alkaline earths.** Iron is completely separated from solutions of the alkali and alkaline earth metals by precipitation with cupferron in dilute mineral acid solutions.<sup>26</sup>

**Iron from phosphorus.** Iron is completely separated from phosphorus by precipitating with cupferron in dilute solutions containing hydrochloric acid.<sup>26</sup>



**Iron from beryllium.** Iron and beryllium can be separated completely by means of cupferron, and beryllium can be determined in the filtrate.<sup>57</sup>

**Iron from gallium.** In solutions in which the acidity is not greater than that corresponding to 6 ml. of sulfuric acid in 400 ml. of solution, gallium and iron are quantitatively precipitated by means of cupferron. This procedure can be used for the separation of gallium from indium. In tartaric acid solutions containing 20 ml. of sulfuric acid in 400 ml. of solution, however, iron and titanium are precipitated with cupferron while gallium remains in solution. In this way iron may be separated from gallium.<sup>58</sup>

**Iron from indium.** Mathers and Prichard<sup>59</sup> have based a procedure for the separation of iron from indium upon the fact that iron is completely precipitated by cupferron in an acid solution, while indium remains in solution. The results obtained using this method are shown in Table 70.

TABLE 70.—SEPARATION OF IRON AND INDIUM

In <sub>2</sub> O <sub>3</sub> Taken g.	Fe <sub>2</sub> O <sub>3</sub> Taken g.	HCl Added ml.	Cupferron Added g.	Final Volume of Sol. ml.	Fe <sub>2</sub> O <sub>3</sub> ppt. by Cupferron g.	In <sub>2</sub> O <sub>3</sub> from Filtrate g.	In <sub>2</sub> O <sub>3</sub> Lost g.
0.0606	None	2	0.24	16	0.0025	0.0598	0.0008
0.0606	0.0363	3	0.60	21	0.0387	0.0598	0.0008
0.0606	None	3	0.24	17	0.0009	0.0586	0.0020
0.0606	0.0726	3	0.60	33	0.0760	0.0587	0.0019
0.0606	0.0726	3	0.60	33	0.0721	0.0603	0.0003
0.0718	None	3	0.24	17	0.0018	0.0695	0.0023
0.0718	None	3	0.24	17	0.0009	0.0698	0.0020
0.0718	0.0726	3	0.60	33	0.0726	0.0690	0.0028

In addition to the above separations, many procedures have been proposed for the elimination of iron by precipitating with cupferron. For example, in spectral analysis it is often desirable to obtain spectra which are free from lines caused by iron. To remove iron from samples of a material such as mineral water, hydrochloric acid and cupferron are added. This method is particularly satisfactory because copper is removed at the same time.<sup>60</sup>

In the determination of lead by the dithizone method, under certain conditions, interference due to iron cannot be eliminated by use of potassium cyanide. Clifford<sup>61,62</sup> has proposed a method whereby the interfering iron is removed with cupferron. The excess cupferron remaining in the solution interferes with the subsequent determination of lead, but this is overcome by destroying cupferron in the residue by heating.

Agostini<sup>63</sup> has used cupferron to remove iron and copper in a procedure for the analysis of tin.

From the above discussion, then, it may be concluded that the use of cupferron for the elimination or separation of iron has proved extremely important in many procedures, but too many other elements are precipitated to make the

determination of iron by this method particularly useful. Copper, lead, silver, mercury, tin and bismuth interfere, although these may be eliminated by precipitation with hydrogen sulfide. In addition titanium, zirconium, cerium, thorium, tungsten, vanadium and other elements interfere with this procedure. In general, it may be stated that the cupferron method for iron does not offer any advantages over the older established methods.

**Detection of iron.** Iron may be detected by the precipitate or color reaction which it yields with cupferron. The test is carried out in a neutral or weakly acid solution. As little as 50 $\gamma$  of iron can be detected in 5 ml. of solution. Copper gives a similar reaction.<sup>138,158</sup>

**Determination of titanium.** Schroeder<sup>64</sup> observed that titanium is quantitatively precipitated from acid solutions by means of cupferron. Bellucci and Grassi<sup>65,66</sup> studied this reaction and found that titanium is quantitatively precipitated as  $(C_6H_5(NO)NO)_4Ti$ , which can be ignited to  $TiO_2$ . Thornton<sup>67-70</sup> has shown that this method for the determination of titanium is capable of producing highly accurate results in solutions containing varying quantities of sulfuric acid and tartaric acid. Complete precipitation is possible from solutions containing as much as 40 per cent by volume of concentrated sulfuric acid. Precipitation must not occur in the presence of high concentrations of nitric acid, due to the effect of the latter upon cupferron. The following method may be used for the determination of titanium in the absence of interfering substances:<sup>66</sup>

**Procedure.** Make the solution containing titanium slightly acid with hydrochloric or sulfuric acid, and then add an excess of a 6 per cent solution of cupferron. The excess is shown by the appearance of a white precipitate, which is caused by the precipitation of nitroso-phenylhydroxylamine. Allow the mixture to stand for several minutes, filter the precipitate, and wash several times with cold water. Dry the residue in a steam oven and ignite and weigh as  $TiO_2$ .

Cupferron has been used by various investigators for the determination of titanium in steel and alloy steel.<sup>71-74</sup> Cunningham<sup>72</sup> has developed a method for the determination of titanium in plain-carbon, high-chromium and 18-8 chromium-nickel steels. The method described here, which is taken from the published work of Cunningham, requires from one to one and one-fourth hours for the complete analysis. This includes the solution of the sample in dilute sulfuric acid, the precipitation of titanium with cupferron in the presence of ferrous iron, filtration, ignition, and the final determination of titanium by a colorimetric method.

**Procedure.** Treat 0.5-1 g. of the sample of drillings in a 150-ml. covered beaker with 100 ml. of 10 per cent sulfuric acid, and heat the liquid gently until all action appears to have ceased. Cool the solution to approximately 20° C., add some ashless paper pulp, and then add dropwise with stirring a cold, freshly prepared, 6 per cent solution of cupferron until the precipitate just assumes a reddish-brown color. Additional cupferron only causes the precipitation of more iron. Filter the precipitate, which contains all the titanium, together with

a small quantity of iron, on an 11-cm. paper containing some ashless paper pulp. Wash 12-15 times with cold 5 per cent sulfuric acid, and then wash 5 times or more with 5 per cent ammonium hydroxide if the steel is known to contain small quantities of molybdenum or tungsten. Transfer the paper and residue to a 50-ml. platinum crucible, and ignite at a temperature just sufficient to destroy the carbon of the filter paper. Fuse the contents of the crucible with approximately 1 g. of potassium pyrosulfate, and dissolve the melt in 25 ml. of 10 per cent sulfuric acid. Transfer the solution to a Camp comparison tube, cool to room temperature, and determine titanium colorimetrically as follows:

Add 3 ml. of 3 per cent hydrogen peroxide, and mix the solution thoroughly. This results in the development of a light straw to amber color, which is proportional in intensity to the amount of titanium present. To another comparison tube, add 25 ml. of cold 10 per cent sulfuric acid, the same amount of potassium pyrosulfate used in making the fusion, 3 ml. of hydrogen peroxide, and then from a 10-ml. buret add a measured amount of standard titanium sulfate solution (1 ml. = 0.0005 g. Ti) which contains slightly less titanium than the sample. Make the volume of the standard equal to that of the sample by the addition of the necessary amount of 10 per cent sulfuric acid. The color of the standard should now be slightly less intense than that of the sample. Then add equal additional volumes of the standard titanium solution and of 10 per cent sulfuric acid to the standard and sample, respectively. Mix the solutions and compare after each addition until the colors of the two solutions match exactly. The per cent of titanium in the steel is found by multiplying the number of ml. of standard titanium sulfate used by 0.0005 and 100 and dividing by the weight of sample.

If the steel contains an appreciable amount of copper, filter the hot sulfuric acid solution of the sample on a 9-cm. paper containing some ashless paper pulp, and wash the filter and contents with 10 per cent sulfuric acid. Cool the filtrate to about 20° C., and carry out the cupferron precipitation as described above.

Transfer the paper containing the sulfuric acid-insoluble metallic copper to a 250-ml. beaker, treat with 25 ml. of nitric acid (d. 1.135) and warm the solution to dissolve the copper. Add approximately 50 ml. of hot water and a slight excess of ammonium hydroxide, and heat the solution to boiling. Filter and wash the paper and precipitate with hot water. Ignite the precipitate at a low temperature to burn off the carbon of the filter paper, add to the ignited cupferron precipitate, and fuse the combined precipitates with potassium pyrosulfate. Dissolve the melt in 10 per cent sulfuric acid, and determine titanium colorimetrically as previously described.

If the steel is known to contain vanadium, transfer the ignited cupferron precipitate to a 100-ml. platinum dish, treat with 5 ml. of 48 per cent hydrofluoric acid and 10 ml. of 60 per cent perchloric acid, and evaporate the solution on a sand bath until the volume is reduced to 5 ml. or less. Any chromium carbide that fails to dissolve during the solution of the sample in sulfuric acid is rendered soluble by the strong fuming with perchloric acid. Dilute the solution with warm water to 50 ml., treat with an excess of 5 ml. of 10 per cent sodium hydroxide,

boil several minutes, and filter on a 9-cm. paper. Wash the paper and precipitate thoroughly with hot water, ignite, fuse with a small quantity of potassium pyrosulfate, and complete the determination of titanium as described above. Vanadium and chromium pass into the filtrate as soluble sodium vanadate and sodium chromate.

If the titanium content of the steel is sufficiently high to make the colorimetric method impractical, carry out the determination as follows:

**Procedure.** Dissolve 1 g. of the sample, and carry out the cupferron precipitation as described above. Transfer the paper and precipitate to a platinum dish, and ignite at a temperature just high enough to destroy the carbon of the paper. Treat the contents of the dish with 5 ml. of 48 per cent hydrofluoric and 10 ml. of 60 per cent perchloric acid, and evaporate the liquid on a sand bath until all perchloric acid is expelled. Fuse the residue with several grams of sodium pyrosulfate, and dissolve the melt in 50 ml. of 10 per cent sulfuric acid. Add an excess of 5 ml. of 10 per cent sodium hydroxide, boil the solution for several minutes, and filter on a 9-cm. paper. Wash the precipitate and paper thoroughly with hot water. Convert any vanadium present to sodium vanadate, which passes into the filtrate. Dissolve the precipitate from the paper with 25 ml. of hot 1:4 sulfuric acid, and wash the filter well with hot water.

Treat the solution (which contains all the titanium) with 1 g. of tartaric acid, make alkaline with ammonium hydroxide, and then make acid with an excess of 2 ml. of sulfuric acid (d. 1.84) per 100 ml. of solution. Saturate the solution with hydrogen sulfide, and if any precipitate forms, filter on a 9-cm. paper containing some ashless paper pulp. Wash thoroughly with hydrogen sulfide water containing 1 per cent sulfuric acid and 1 per cent tartaric acid, and discard. Add an excess of 2 ml. of ammonium hydroxide (d. 0.90) to the filtrate, and pass hydrogen sulfide through the solution for an additional 5 minutes. Add some ashless paper pulp, filter the solution on a 9-cm. paper, and wash the precipitate of ferrous sulfide thoroughly with ammonium sulfide water containing 1 per cent ammonium sulfate and 1 per cent ammonium tartrate, and discard. Boil the filtrate, which should have a volume of about 150 ml., to expel hydrogen sulfide, acidify with an excess of 30 ml. of 1:1 sulfuric acid, and cool to 20° C. Add some ashless paper pulp and precipitate titanium by the dropwise addition, with constant stirring, of a cold, freshly prepared, 6 per cent solution of cupferron. An excess of the reagent is indicated by the formation of a snow-white precipitate which rapidly disappears. Filter the titanium precipitate on an 11-cm. paper containing some ashless paper pulp, wash 12-15 times with cold 5 per cent sulfuric acid, and then 5 times with 5 per cent ammonium hydroxide. Transfer the paper and precipitate to a platinum crucible, and ignite, first at a low temperature, and finally at 1050-1100° C., and then cool and weigh. The per cent of titanium in the steel is obtained by multiplying the weight of titanium oxide found by 59.95 and dividing by the weight of sample taken.

As an alternative method, fuse the titanium oxide with a small amount of potassium pyrosulfate, dissolve the melt in 100 ml. of 6 per cent sulfuric acid, and

pass the warm solution (about 75° C.) through a zinc reductor into a ferric sulfate solution (prepared by dissolving 100 g. of ferric sulfate in 150 ml. of phosphoric acid (d. 1.72) and 850 ml. of water containing 20 ml. of 1:1 sulfuric acid), and titrate the resulting ferrous sulfate with standard 0.005 N potassium permanganate (1 ml. = 0.002395 g. titanium). First, pass approximately 100 ml. of 2.5 per cent sulfuric acid through the reductor [12 in. (30.5 cm.) in length by 0.75 in. (19.1 mm.) in diameter] and discard. Then pass the hot 6 per cent sulfuric acid solution containing the titanium through the reductor into 25 ml. of ferric sulfate solution and wash the reductor with three 30-ml. portions of hot 6 per cent sulfuric acid, and one 30-ml. portion of water to remove the last traces of titanium. When the titanium solution is passed through the reductor, the tip of the reductor tube should dip beneath the surface of the ferric sulfate solution. Run a blank on the reductor in exactly the same way as in the determination, except that the same volume of 6 per cent sulfuric acid is substituted for the titanium solution.

Dymov and Volodina<sup>73</sup> have used cupferron for the determination of titanium in stainless steels. Titanium, along with vanadium, aluminum and phosphate, is separated from chromium, nickel, iron, cobalt and copper by electrolysis; and titanium and vanadium are then precipitated with the aid of cupferron. The precipitate is ignited and fused with sodium carbonate, the melt treated with hot water, the titanium filtered off, and after dissolving in 50 per cent hydrochloric acid is again precipitated with cupferron. Vanadium is determined in the filtrate by the addition of sulfuric acid and cupferron.

Silverman<sup>74</sup> has proposed to determine titanium in alloy steels by precipitating with cupferron, dissolving the precipitate in sulfuric acid, and determining the titanium colorimetrically. Since cupferron precipitates titanium, iron, copper and zirconium in an acid solution, the solution of the sample is so prepared that only a small amount of iron remains with the titanium precipitate. Zirconium gives no color with hydrogen peroxide, which is used for developing the color with titanium; copper is usually not present in sufficient quantity to cause interference. The size of the sample used depends upon the amount of titanium which it contains: a 5 g. sample is used if the titanium content is less than 0.1 per cent, while a 2 g. sample is used if the percentage ranges from 0.1 to 0.6.

**Procedure.** Transfer the weighed sample of the steel to be analyzed to a 400-ml. beaker and dissolve with the aid of heat in 100 ml. of water and 50 ml. of concentrated hydrochloric acid. Cool, preferably with ice, and dilute to 250 ml. Dissolve about 0.30 g. of cupferron in 15-20 ml. of cold water, and add this to the cold solution containing the sample. Stir and allow the mixture to stand for 5 minutes, and then filter through paper. Wash several times with cold 1:10 hydrochloric acid until the washings come through colorless, and then wash once with cold water.

Place the filter in the beaker which was used for the original precipitation and add 15-20 ml. of concentrated nitric acid and 15 ml. of sulfuric acid. Heat until fumes of sulfuric acid appear and condense on the walls of beaker. If the solution still remains yellow in color, remove the beaker from the hot plate and add 5-10 drops of concentrated nitric acid, and again heat until fumes appear,

The solution should remain colorless or slightly green in color. Add cold water to the cooled acid solution and again cool, and then add 5 ml. of hydrogen peroxide. The titanium solution should contain about 5 per cent of sulfuric acid.

The final color comparison can be made by matching against standard titanium solutions in a colorimeter; by preparing standards containing 0.1, 0.2, 0.3 per cent, etc., of titanium solution and diluting the unknown to match one of these standards; or the unknown solution may be diluted to a definite volume and the color of this solution matched with a 5 per cent sulfuric acid solution containing 2 ml. of hydrogen peroxide to which is added known quantities of a standard titanium solution.

By following the above procedure, iron, chromium and nickel do not interfere. By dissolving the sample in hydrochloric acid, the greater part of the iron remains in the ferrous state and the ferrous iron, chromium and nickel are washed out with the dilute acid. The above procedure is claimed to be more rapid than that used by Barton<sup>75</sup> and recommended by Scott.<sup>76</sup>

Insoluble vanadium carbide may remain in the cupferron precipitate. In this case, the solution shows a brown color after treating with hydrogen peroxide if the vanadium concentration is greater than 0.2 per cent. If this occurs, titanium must be reprecipitated with cupferron and vanadium removed by filtration.

Cupferron has proved useful for the separation and determination of titanium in the analysis of many special materials. Brown<sup>45</sup> has used cupferron for the precipitation of titanium in the analysis of zirconium minerals. Lundell and Knowles<sup>77</sup> have also used this method for the determination of titanium in zirconium ores. It is worthy of mention that chromium and nickel do not interfere in the precipitation of titanium and zirconium with cupferron, and that in this scheme tungsten does not interfere, since it is removed before the final precipitation. Vanadium, if present, would require a special treatment, but since this element has not been reported in the analysis of zirconium ores, and since its presence in considerable quantities would be indicated at various points in the analysis, it should cause no trouble.

Shportenko<sup>78</sup> and Bennett<sup>156</sup> have used cupferron for the determination of titanium in ores. Waddell<sup>79</sup> has also suggested a similar procedure for the rapid estimation of titanium in iron ores, and Melent'ev and Terekhovko<sup>80</sup> have used cupferron for the precipitation of titanium, columbium and tantalum in mineral analysis. Schoklitsch<sup>89</sup> has used cupferron for the separation of iron and titanium from silicate minerals. Milner and co-workers<sup>149</sup> have used cupferron in the determination of titanium in corrosion-resistant steels.

Gal'perin<sup>152</sup> has used cupferron to separate titanium as a preliminary to the colorimetric determination of titanium in steel by the hydrogen peroxide method.

**Separation of titanium. Titanium from aluminum.** Bellucci and Grassi<sup>65</sup> have studied the precipitation of titanium in the presence of aluminum, and have shown the separation to be quantitative. The following procedure may be used:

**Procedure.** Make the solution to be analyzed acid with sulfuric or hydrochloric acid, and treat with a 6 per cent solution of cupferron until a white pre-

precipitate, which appears above the yellow titanium precipitate, indicates an excess of the reagent. Filter the precipitate, dry on a water-bath and ignite to  $\text{TiO}_2$  in a crucible. It is not necessary to wash the precipitate with ammonium hydroxide as in the determination of iron since an excess of cupferron does not interfere. It is not necessary to filter the precipitate immediately. In separating aluminum from titanium by this method, the precipitate should be washed with dilute hydrochloric acid.

Good results are obtained when titanium and aluminum are in the molecular ratio of 1:50. Thornton<sup>67-69</sup> has confirmed the claims of Bellucci and Grassi,<sup>65</sup> but has found that the separation is clear only in highly acid solutions, and that better results are obtained by the addition of tartaric acid. The results obtained with this method are reported in Table 71.

TABLE 71.—SEPARATION OF TITANIUM AND ALUMINUM

$\text{TiO}_2$ Used g.	$\text{Al}_2\text{O}_3$ Used g.	$\text{TiO}_2$ Found g.	Error g.	$\text{H}_2\text{SO}_4$ (1:1) ml.	Tartaric Acid Used g.	Volume of Solution ml.
.1066	.1127	.1179	+.0113	5	...	200
.1066	.1127	.1094	+.0028	10	...	200
.05715	.1127	.0590	+.0018	5	1.2	200
.0572	.1127	.0577	+.0005	10	1.2	200
.0575	.1127	.0579	+.0004	15	1.2	200
.0573	.1127	.0575	+.0002	20	1.2	200
.1067	.1127	.1072	+.0005	20	1.5	400
.1068	.1127	.1070	+.0002	20	1.5	400

Lundell and Hoffman<sup>48</sup> have used cupferron for the elimination of iron, titanium and zirconium in the analysis of bauxite and refractories of high aluminum content. von Bergkampff<sup>81</sup> has used a procedure for separating iron, titanium and aluminum in which titanium is precipitated by means of cupferron. In this procedure the iron is reduced with hydrogen sulfide and is precipitated in an ammoniacal tartrate solution by the addition of ammonium sulfide. The mixture is filtered, and the titanium in the filtrate is precipitated with cupferron after acidification. Zirconium, vanadium and gallium are precipitated along with titanium in the above separation.

Raeder and Lyshoel<sup>148</sup> use cupferron to precipitate iron and titanium as a preliminary to the determinations of aluminum, and Hammarberg and Phragmen<sup>151</sup> separate titanium, iron and vanadium as a preliminary to the determination of aluminum in steel.

Hoffman and Lundell<sup>54</sup> have used cupferron for the precipitation of iron, vanadium, titanium, zirconium, tin and gallium from solutions of aluminum salts in order to obtain high purity aluminum.

Brown<sup>45</sup> has used cupferron for the separation of iron, titanium and zirconium from aluminum salts. Precipitation is carried out in cold solutions containing 25 ml. of 1:1 sulfuric acid in 150 ml. of solution.

**Titanium from iron.** The separation of titanium from iron can be accomplished in an ammoniacal tartrate solution by the reduction of iron and precipitation by the addition of hydrogen sulfide. Copper, cobalt and zinc, if present, are also precipitated quantitatively with iron. After separating iron from titanium by the ammoniacal tartrate-hydrogen sulfide method, the filtrate is acidified, the hydrogen sulfide expelled, and titanium precipitated in the presence of aluminum and phosphorus by means of cupferron. The following method is described by Thornton: <sup>67-69</sup>

**Procedure.** To the sample solution, which should have a volume not greater than 100 ml., add a quantity of tartaric acid which is at least 4 times the aggregate weight of the 4 oxides to be held in solution. Carefully neutralize with ammonium hydroxide and acidify with 2 ml. of 1:1 sulfuric acid. Add hydrogen sulfide to the solution until the latter is colorless. Then add an excess of ammonium hydroxide, and again add hydrogen sulfide until iron is completely precipitated and the solution is left alkaline. Filter off the ferrous sulfide, and wash 10 times with very dilute, colorless ammonium sulfide. Add 40 ml. of 1:1 sulfuric acid to the filtrate, and boil to expell all hydrogen sulfide. Cool to room temperature and dilute to 400 ml.

Add a 6 per cent solution of cupferron slowly and with constant stirring, and then allow to stand. Test for completeness of precipitation with a few drops of the cupferron solution. If a white precipitate forms, an excess of the reagent is indicated, but if a yellow precipitate forms, precipitation is incomplete. Collect the precipitate on paper, using gentle suction, and wash 20 times with a solution prepared by diluting 100 ml. of hydrochloric acid (d. 1.20) to 1 liter. Dry with suction, and transfer to a platinum or porcelain crucible, and dry at 110° C. With the crucible not quite covered, begin the ignition over a very small flame, and after a little while increase the temperature. Finally, ignite to constant weight over a Meeker burner. Weigh as  $\text{TiO}_2$ .

Results obtained using this method are shown in Table 72.

TABLE 72.—SEPARATION OF TITANIUM FROM IRON, ALUMINUM, AND PHOSPHORUS

$\text{TiO}_2$ Taken g.	$\text{Fe}_2\text{O}_3$ Taken g.	$\text{Al}_2\text{O}_3$ Taken g.	$\text{P}_2\text{O}_5$ Taken g.	$\text{TiO}_2$ Found g.	Error g.	$\text{H}_2\text{SO}_4$ 1:1 ml.	Tartaric Acid g.	Volume of Solution ml.
0.1065	0.2036	0.1127	0.0154	0.1070	+0.0005	30	2	400
0.1066	0.2036	0.1127	0.0151	0.1068	+0.0002	30	2	400
0.1065	0.1018	0.1127	0.0153	0.1067	+0.0002	40	2	400
0.1067	0.1018	0.1127	0.0153	0.1069	+0.0002	40	2	400
0.1066	0.2267	0.2254	0.0153	0.1069	+0.0003	40	2.5	400
0.1066	0.2267	0.2254	0.0153	0.1073	+0.0007	40	2.5	400

**Titanium from phosphorus.** Phosphoric acid is without serious effect in the determination of titanium with cupferron if the precipitation is carried



out in strongly acid solution.<sup>87-69</sup> Lundell and Knowles,<sup>85</sup> however, claim that the contamination is greater than that shown by Thornton,<sup>87-69</sup> but attribute this difference in result to the presence of zirconium, which forms the more insoluble phosphate. Ridsdale<sup>82</sup> has used cupferron for the separation of phosphorus from titanium in the determination of phosphorus in hematite ore. Titanium is removed since it interferes with the subsequent determination of phosphorus.

**Titanium from iron, aluminum and phosphorus.** The procedure described above by Thornton<sup>87-69</sup> for separating iron from titanium may be applied to the separation of titanium from iron, aluminum and phosphorus.

**Titanium from platinum.** Since platinum is often introduced into titanium solutions by fusion operations, Thornton<sup>87-69</sup> investigated the effect of chloroplatinic acid upon the analysis of titanium solutions, and has found the platinum to be without effect. Gilchrist and Wichers<sup>88</sup> have used cupferron for the elimination of titanium in the analysis of the platinum metals.

**Titanium from boric acid.** Since borax is used for the fusion of some ores, a number of tests were made by Knowles and Lundell<sup>85</sup> to determine what, if any, effect boric acid had upon the titanium determination. The presence of boric acid was found to be without any effect.

**Titanium from alkali metals.** Tests made by Lundell and Knowles<sup>85</sup> have confirmed the observation of Thornton and Hayden<sup>84</sup> that the presence of excessive quantities of alkali salts causes high values in the precipitation of zirconium and titanium by means of cupferron. This interference may be eliminated by precipitating with ammonium hydroxide, dissolving in acid and then precipitating the titanium with cupferron.

**Titanium from silica.** The separation of titanium and zirconium from silica by means of cupferron is not complete.<sup>85</sup> Silica may be volatilized with hydrogen fluoride in the final ignited precipitate without loss of titanium or zirconium, provided a sufficient quantity of sulfuric acid is present.

**Titanium from vanadium.** According to Lundell and Knowles,<sup>85</sup> it is impossible to separate titanium and zirconium from vanadium in either the tetravalent or pentavalent form.

**Titanium from uranium.** Hexavalent uranium does not interfere with the precipitation of titanium with cupferron, but tetravalent uranium must not be present.<sup>85,86</sup>

**Titanium from tungsten.** Tungsten interferes seriously in the precipitation of titanium and zirconium by means of cupferron.<sup>85</sup>

**Titanium from thorium.** Lundell and Knowles<sup>85</sup> report that it is not possible to separate titanium and zirconium from thorium by means of cupferron.

**Titanium from cerium.** Tetravalent cerium interferes considerably in the precipitation of titanium and zirconium with cupferron, but tetravalent cerium interferes only slightly.<sup>85</sup>

**Titanium from gallium.** Brukl<sup>86</sup> reports that gallium and titanium may be separated by neutralizing the mixture of the two metals with ammonium hydroxide and adding an excess of ammonium oxalate. This solution is then made 1 N in oxalic acid and titanium precipitated in the cold solution by means of cupferron. The precipitate is ignited and weighed as  $TiO_2$ . The oxalate is destroyed in the filtrate by heating with hydrogen peroxide and sulfuric acid, and gallium is then precipitated with cupferron in the cold after diluting with water. von Bergkamp<sup>88</sup> has also used cupferron for the separation of gallium and titanium. In tartaric acid solutions containing 20 ml. of sulfuric acid in 400 ml. of solution, iron and titanium can be precipitated while the gallium remains in solution.

**Detection of titanium.** Titanium may be detected by the reaction which it gives with cupferron. Tin, columbium, tantalum, vanadium, thorium, cerium, zirconium, iron and copper interfere.

**Determination of zirconium.** Schroeder<sup>84</sup> observed that zirconium is precipitated quantitatively by cupferron in acid solutions. Thornton and Hayden<sup>84,87-89</sup> have shown that the determination can be carried out in solutions containing 5.0-7.5 per cent by volume of sulfuric acid, and Lundell and Knowles<sup>85</sup> found that zirconium is quantitatively precipitated from solutions containing as much as 40 per cent by volume of sulfuric acid, and that tartaric acid is without effect upon the precipitation.

The conditions necessary for the precipitation of zirconium by cupferron are essentially the same as those used in precipitating titanium. The following procedure is used for the determination of zirconium:<sup>90</sup>

**Procedure.** Acidify a solution containing zirconium with sulfuric acid and add a 6 per cent aqueous solution of cupferron at ordinary temperature. A white flocculent precipitate is formed. The cupferron reagent is added until an excess is indicated by the formation of white nitrosophenylhydroxylamine. Filter, wash with cold water and dilute ammonium hydroxide, and then dry in a platinum crucible at 100° C. Heat the residue slowly at first and finally at red heat to convert to  $ZrO_2$ .

Lundell and Knowles<sup>91</sup> have developed a method for the analysis of steel in which zirconium is determined by precipitation with cupferron. In this procedure zirconium and titanium are precipitated with cupferron after the removal of iron, and the mixed oxides of zirconium and titanium are weighed. Zirconium is then determined after estimating titanium colorimetrically.

Lundell and Knowles<sup>77</sup> and Brown<sup>45</sup> have used cupferron for the determination of zirconium in zirconium ores.

Coppieters<sup>92</sup> has studied the cupferron method of determining zirconium, and reports that it is capable of excellent results, but that its usefulness is limited by its lack of specificity.

**Separation of zirconium. Zirconium from aluminum.** Zirconium can be quantitatively separated from aluminum by precipitation with cupferron, but the precipitate always contains a little phosphoric acid when the latter is

present in the solution. Phosphoric acid is best removed by fusion with sodium carbonate.<sup>45,67-69,84,87-89,93,94</sup>

**Zirconium from iron.** Cupferron can be used for the precipitation of zirconium after removing iron by reducing with hydrogen sulfide and precipitating as ferrous sulfide.<sup>67-69,84,87-89,94</sup>

**Zirconium from iron and aluminum.** Thornton and Hayden<sup>67-69,84,87-89</sup> have shown that zirconium can be determined in the presence of aluminum after separating iron by precipitation as ferrous sulfide.

**Procedure.** To the solution containing zirconium, iron and aluminum, add a quantity of tartaric acid which is equal to 5 times the weight of the three metals calculated as the oxides. The volume of this solution should not exceed 100 ml. Add ammonium hydroxide until the solution is neutral to litmus, and then add 2 ml. of 1:1 sulfuric acid. Treat with hydrogen sulfide to reduce the iron, make slightly ammoniacal, and then treat with hydrogen sulfide until all the iron is precipitated. Make certain that the mixture is still alkaline to litmus. Filter, wash the precipitate about ten times with colorless ammonium sulfide solution, and acidify the filtrate with 40-60 ml. of 1:1 sulfuric acid and boil until all hydrogen sulfide is expelled. Cool the solution with ice water, dilute to 400 ml. and add an excess of 6 per cent aqueous solution of cupferron gradually and with stirring. Filter immediately through paper, using mild suction. Wash 20 times with a dilute solution of hydrochloric acid prepared by diluting 100 ml. of concentrated acid to 1 liter. Place the precipitate with the paper in a platinum crucible and dry at 110° C., and then ignite over a Meeker burner and weigh as  $ZrO_2$ .

Hoffman and Lundell<sup>54</sup> have used cupferron for the elimination of iron, vanadium, titanium, zirconium, tin and gallium in the preparation of pure samples of aluminum. Lundell and Hoffman<sup>48</sup> have also used cupferron for the precipitation of iron, titanium, zirconium and vanadium in the analysis of bauxite and refractories of high aluminum content.

**Zirconium from phosphorus.** Thornton and Hayden<sup>84,87-89</sup> originally reported that the separation of zirconium from phosphoric acid by precipitating the former with cupferron is impossible, but Lundell and Knowles<sup>85</sup> have found that fair separations are possible if the acidity is maintained as high as 10 per cent sulfuric acid by volume and the concentration of  $P_2O_5$  does not exceed 0.02 g. per 400 ml. of solution. Higher phosphate concentrations require a preliminary removal, or a correction which is to be applied after the analysis.

**Zirconium from boric acid.** Same as analysis of titanium (page 378).

**Zirconium from alkali salts.** Thornton and Hayden<sup>84,87-89</sup> report that a moderate excess of alkali salts causes no difficulty in the determination of zirconium by the cupferron method.

**Zirconium from silica, vanadium, uranium, tungsten, thorium and cerium.** Same as titanium (page 378).

**Zirconium from manganese.** Brown<sup>45</sup> has used cupferron for the separation of zirconium from solutions containing manganese.

**Zirconium from uranium.** Angeletti<sup>90</sup> has used cupferron for the precipitation of zirconium in the presence of uranium. Zirconium is precipitated from an acid solution in the usual manner, and uranium is precipitated in the filtrate by means of ammonium hydroxide.

**Determination of thorium.** Thornton<sup>95</sup> has studied the use of cupferron as a precipitant for thorium, and has found that precipitation is incomplete, even in the presence of small quantities of sulfuric acid. Good results are obtained, however, by precipitating thorium from a solution containing a large quantity of ammonium acetate. Lundell and Knowles<sup>85</sup> confirm the findings of Thornton.

The conditions which are most suitable for the precipitation of thorium are as follows: to 500 ml. of solution containing approximately 0.1 g. of  $\text{ThO}_2$ , add 15 g. of ammonium acetate and 1.25 ml. of 1:1 sulfuric acid. Precipitate with a 6 per cent aqueous solution of cupferron. Thornton<sup>95</sup> has found that thorium can be determined in iron and thorium salts by a preliminary removal of iron as ferrous sulde by precipitating with ammonium sulfide in an ammoniacal tartrate solution. Thorium is precipitated in the filtrate with cupferron from a buffered acetate solution. Matveev<sup>96</sup> has used a similar method for separating iron from thorium.

The elements which interfere with the determination of thorium are the same as those encountered in the determination of titanium, and probably the interference is greater because of the low acidity at which the thorium precipitation must necessarily be carried out. Further, the determination of thorium by precipitating with cupferron appears to be of no practical importance, since it is affected by as many interfering elements as in the ammonium hydroxide precipitation of this element.

**Detection and determination of vanadium.** Rodeja<sup>97</sup> has shown that acid solutions of the alkali metavanadates react with cupferron to give a red precipitate which is somewhat soluble in water. As little as .001 mg. of vanadium per ml. gives a reddish coloration which changes to green. Rodeja claims that this reaction is more sensitive as a qualitative test than the well-known potassium thiocyanate or hydrogen peroxide reactions. In a further study, Rodeja<sup>98</sup> claims that cupferron does not quantitatively precipitate vanadic salts in dilute acid solutions but that vanadyl salts are quantitatively precipitated.

Turner,<sup>99</sup> in an attempt to separate vanadium from uranium, found that metavanadate is completely precipitated by cupferron in 1 per cent hydrochloric or sulfuric acid solutions, and that the washed precipitate can be ignited to  $\text{V}_2\text{O}_5$ .

**Procedure.** Dilute 25 ml. of the metavanadate solution, containing approximately 0.17 g. of  $\text{V}_2\text{O}_5$  in 200 ml., and add an excess of a 6 per cent aqueous solution of cupferron. Filter the precipitate on paper, wash with a 1 per cent sulfuric acid solution containing 1.5 g. of cupferron per liter, ignite the precipitate in a platinum crucible and weigh as  $\text{V}_2\text{O}_5$ .

Good results are claimed only by observing the following precautions:

- (a) A gradual ignition of the precipitate with a final thorough exposure to air to insure complete oxidation.
- (b) The precipitation must be carried out in a solution which contains approximately 1 per cent hydrochloric or sulfuric acid.
- (c) The temperature must be below 20° C., since a higher temperature or a delay in filtering causes the formation of a gummy mass which makes filtering impossible.

The results obtained by Turner<sup>90</sup> are given in Table 73.

TABLE 73.—DETERMINATION OF VANADIUM

V <sub>2</sub> O <sub>5</sub> Used g.	* V <sub>2</sub> O <sub>5</sub> Found g.	Error g.
0.1655	0.1655	0.000
0.1655	0.1657	+0.0002
0.1655	0.1652	-0.0003
0.1655	0.1658	+0.0003

The results obtained by Turner lead him to conclude that Rodeja's statement concerning the incomplete precipitation of vanadic salts by cupferron was incorrect.

Raeder and Aakre<sup>147</sup> report that both tetravalent and pentavalent vanadium are quantitatively precipitated with cupferron from acid solutions containing respectively 0.31-1.0 and 0.35-4.0 g. of sulfuric acid per 200 ml. of solution. Vanadium cannot, however, be separated from titanium or aluminum in this way.

The most favorable conditions for the precipitation of vanadium with cupferron requires a solution which contains 1 per cent hydrochloric or sulfuric acid, with the element in the pentavalent or tetravalent state, and the precipitate must be washed with 1 per cent acid containing cupferron.

Several procedures have been developed which employ conferron as a precipitant for vanadium in the analysis of steel and iron and alloys.<sup>73,100,101</sup>

Vanadium can be determined nephelometrically or colorimetrically at concentrations of 0.001 mg. per ml. and higher in the presence of 6-7 times as much chromium by reacting with cupferron and stabilizing the suspension with 2 per cent gum arabic.<sup>102</sup>

**Procedure.** To a solution of V<sub>2</sub>O<sub>5</sub>, which must be free from iron, titanium and fluorides, and any undecomposed sodium peroxide used in preparing the sample, add dilute sulfuric acid until neutral to litmus paper. If any precipitate forms, filter and add to each 10 ml. of the solution 1 ml. of concentrated sulfuric acid, and 2 ml. of 25 per cent potassium sulfate if the solution contains no salts of the alkali metals. In the presence of a large excess of chromium, add a few drops of 3 per cent hydrogen peroxide and heat to boiling. Cool and

dilute the cold solution to a definite volume, and use an aliquot portion of this solution for the final determination. For each 10 ml., add 1 ml. of 2 per cent gum arabic solution, and 1 ml. of a 1 per cent cupferron solution which has been decolorized by filtration through activated charcoal. Stir the mixture and then complete the determination by a nephelometric or colorimetric comparison, using a standard solution similarly prepared.

Zinc, cadmium, lead, mercury, manganese, aluminum, phosphoric acid, arsenious acid and boric acid do not interfere.

Bertrand<sup>103</sup> has proposed a scheme for determining vanadium in plants by dissolving the complex formed with cupferron in chloroform. By means of this procedure as little as 0.04 mg. of vanadium can be determined. The extraction with chloroform is made from a solution having a pH of 1.8. Iron, titanium and cerium interfere with this procedure, but can be removed by precipitating with ammonium hydroxide and hydrogen peroxide. Copper must be removed by precipitating with hydrogen sulfide.

A solution of the vanadium complex of cupferron in butyl acetate is brown in color. This may be used for the colorimetric determination of vanadium, although the color fades rapidly.<sup>140</sup>

The vanadium reaction with cupferron may also be used for the detection of the metal.<sup>154</sup>

**Separation of vanadium.** Rodeja<sup>98</sup> has shown that cupferron may be used for a satisfactory separation of vanadium from phosphorus. This is accomplished as follows: Acidify the solution containing vanadium and phosphorus with sulfuric acid, boil with sulfur dioxide to reduce vanadium, and remove the sulfur dioxide with carbon dioxide. Precipitate vanadium with cupferron, wash with dilute sulfuric acid, and ignite to vanadium pentoxide.

According to Turner,<sup>104</sup> vanadium can be separated from arsenic acid by precipitating vanadium with cupferron. Unlike the procedure of Rodeja, that employed by Turner does not involve the reduction of vanadium, but simply the precipitation of the metal with cupferron according to the procedure given on page 381. The only change in this procedure is that a more thorough washing is required. Turner<sup>104</sup> has also described a procedure for the separation of vanadium from uranium when both elements are present in a sulfuric acid solution as the vanadate and hexavalent uranium. This procedure allows for the presence of arsenic, phosphorus, aluminum, calcium and magnesium. A solution containing 10 per cent by volume of concentrated sulfuric acid is suitable for this separation. Iron, titanium and zirconium, if present, are precipitated with vanadium. Auger<sup>105</sup> suggests that the uranium which is present in the filtrate after the vanadium precipitation can be precipitated quantitatively by reduction to the tetravalent state, in which form it is completely precipitated as  $U(C_6H_5N_2O_2)_4$  by cupferron in sulfuric acid solution.

Holladay and Cunningham<sup>106</sup> have studied the methods of Turner<sup>104</sup> and Auger,<sup>105</sup> and have confirmed Auger's statement that tetravalent uranium is quantitatively precipitated by cupferron in sulfuric acid solution. Holladay and Cunningham<sup>106</sup> have used the following method for the separation and determination of vanadium:

**Procedure.** Acidify 100 ml. of the solution containing vanadium, uranium, aluminum, calcium, magnesium, phosphorus and zinc with 12 ml. of concentrated sulfuric acid, treat with sufficient 0.1 N potassium permanganate to give a permanent pink color and cool to 10° C. Precipitate vanadium in the usual manner by adding an excess of cold 6 per cent cupferron solution in the presence of paper pulp, filter, and wash with cold 10 per cent sulfuric acid containing 1.5 g. of cupferron per liter.

Place the filter containing the cupferron precipitate in an Erlenmeyer flask, and add 30 ml. of concentrated sulfuric acid and 10 ml. of nitric acid, and then evaporate until fumes appear. Repeat the evaporation several times using 10-ml. portions of nitric acid to destroy all carbonaceous matter, and then evaporate once with 10 ml. of water to expel every trace of nitric acid. Reduce the vanadium with hydrogen peroxide and titrate with 0.05 N potassium permanganate according to the method of Cain and Hostetter.<sup>107</sup> The oxidation corresponds to the conversion of  $V_2O_4$  to  $V_2O_5$ . 1 ml. of 0.05 N  $KMnO_4$  = 0.00255 g. of V.

The separation of vanadium in solutions containing moderate or large amounts of tungsten may be accomplished by precipitating vanadium with the aid of cupferron:<sup>108,109</sup>

**Procedure.** Add 10 ml. of reagent hydrofluoric acid to 200 ml. of a sulfuric acid solution of vanadic and tungstic acids, and then neutralize the mixture with ammonium hydroxide. Add 20 ml. of hydrochloric acid and dilute the solution to 300 ml. Cool the mixture and add 1 g. of cupferron dissolved in 20 ml. of water. If only a small quantity of vanadium is present, add 50 g. of ammonium chloride to the solution, and increase the amount of hydrochloric acid to 25 ml. Precipitate as above, ignite the precipitate, heat with a fusion mixture of alkali carbonates and dissolve in water, and then reduce vanadium with sulfurous acid and titrate with potassium permanganate in the usual way, or determine vanadium colorimetrically with hydrogen peroxide according to the method of Meyer and Pawletta.<sup>140</sup>

Hoffman and Lundell<sup>54</sup> have used cupferron for the elimination of vanadium in the preparation of pure samples of aluminum, and Hammarberg and Phragmen<sup>151</sup> have used the reagent for the removal of vanadium in the determination of aluminum in steel.

**Determination of uranium.** Uranium in the tetravalent state may be quantitatively precipitated with cupferron from solutions containing 4-8 per cent of sulfuric acid. The precipitate of  $U(C_6H_5N_2O_2)_4$  may be quantitatively converted by ignition to  $U_3O_8$ .

The determination of uranium after precipitation with cupferron has been of interest chiefly in processes which require the separation of uranium from vanadium (see previous section). The separation of vanadium from uranium, when both elements are present in sulfuric acid solution as the vanadate and hexavalent uranium, was first described by Turner.<sup>104</sup> He applied the separation

to the determination of vanadium in carnotite. A solution containing 10 per cent by volume of concentrated sulfuric acid is suitable for this separation. Iron, titanium and zirconium are also precipitated with vanadium, and hence may be separated from uranium by this procedure. Auger<sup>105</sup> has suggested that uranium can be determined in the filtrate after the vanadium separation by first reducing to the tetravalent state, and then precipitating by cupferron in the sulfuric acid solution. Holladay and Cunningham<sup>106</sup> have studied the procedures of Turner<sup>104</sup> and Auger,<sup>105</sup> and have confirmed Auger's statement that tetravalent uranium is quantitatively precipitated by cupferron in a sulfuric acid solution, and that the cupferron precipitate can be ignited to  $U_3O_8$ . Further, they have shown that uranium can be quantitatively separated from aluminum, calcium, magnesium, phosphorus and zinc by a proper control of the acidity of the solution. The following procedure may be used for the separation of uranium from vanadium and the final determination of uranium:

**Procedure.** Acidify 100 ml. of the solution containing uranium and vanadium, aluminum, calcium, magnesium, phosphorus and zinc with 12 ml. of concentrated sulfuric acid, and then add sufficient 0.1 N potassium permanganate to impart a permanent pink color to the solution. Cool the mixture to 10° C. and precipitate vanadium in the presence of a little paper pulp with an excess of cold 6 per cent cupferron solution. Filter, and wash the precipitate with a cold 10 per cent sulfuric acid solution containing 1.5 g. of cupferron per liter. Add the washings to the filtrate.

Evaporate the filtrate and washings to a volume of about 50 ml. and add 20 ml. of concentrated nitric acid, and again evaporate until fumes of sulfur trioxide are evolved. Evaporate the mixture a second time with nitric acid to destroy all organic matter, and then evaporate with 10 ml. of water to remove all nitric acid. Dilute the solution with a volume of water necessary to give the desired acidity (137 ml. of water gives an acidity of 8 per cent), cool to room temperature, and pass the solution through a Jones reductor to reduce uranium. Wash the reductor with 100 ml. of sulfuric acid of the same acidity as that of the solution containing the uranium. Cool the solution of tetravalent uranium to 5-10° C. and add an excess of a freshly prepared 6 per cent solution of cupferron.

Add a little ashless paper pulp and filter the brown precipitate on an 11-cm. filter paper. Wash the precipitate of  $U(C_6H_5N_2O_2)_4$  with cold 5 per cent sulfuric acid containing 1.5 g. of cupferron per liter, and ignite in a platinum crucible, first at a low temperature and finally at 1000-1050° C. in an electric furnace into which a current of oxygen is passed. Cool the crucible and contents, and weigh as  $U_3O_8$ .

The precipitate may be fused with potassium pyrosulfate, dissolved in 100 ml. of 6 per cent sulfuric acid, and the uranium determined, after passing the cold solution through a Jones reductor, by titrating with 0.1 N potassium permanganate solution.

Results obtained using the above procedure are given in Table 74.



TABLE 74.—SEPARATION OF URANIUM AND VANADIUM

H <sub>2</sub> SO <sub>4</sub> Per Cent	Uranium		Found Titrimetric g.	Vanadium		Phosphorus		Wt Al <sub>2</sub> O <sub>3</sub> Added g.
	Added As U <sub>3</sub> O <sub>8</sub> g.	Found As U <sub>3</sub> O <sub>8</sub> g.		Added g.	Found g.	Added g.	Found g.	
2	0.2105	0.2188	0.2108	.....	.....	0.00057	.....	0.1140
3	0.2105	0.2137	0.2097	.....	.....	0.00057	.....	0.1140
4	0.1684	0.1679	0.1675	.....	.....	0.00114	0.00114	0.1980
5	0.0318	0.0316	0.0314	0.0260	0.0260	.....	.....	0.0760
6	0.0635	0.0628	0.0622	0.1300	.....	.....	.....	0.1885
6	0.0635	0.0625	0.0624	0.1010	0.1022	0.00114	0.00112	0.1885
6	0.0635	0.0636	0.0628	0.0203	0.0203	0.00342	0.00340	0.1885
6	0.4210	0.4210	0.4194	.....	.....	0.00285	0.00284	0.1885
6	0.2105	0.2103	0.2100	.....	.....	0.00285	0.00288	0.1885
8	0.4210	0.4208	0.4200	.....	.....	0.00285	0.00285	0.0580
8	0.1684	0.1688	0.1681	.....	.....	0.00114	0.00116	0.1980

**Detection of uranium.** Martini<sup>186,187</sup> and Isakov<sup>184</sup> have used the reaction with cupferron as the basis for the microchemical detection of uranium. The method is not very sensitive (1:1000), and copper, cadmium, iron, and the alkaline earth metals interfere.

**Determination of gallium.** Gallium can be quantitatively precipitated by cupferron in solutions which are 0.6 N in sulfuric acid, provided an excess of 15-20 ml. of 6 per cent cupferron is added.<sup>110</sup> The precipitate can be converted to  $Ga_2O_3$  by treating with nitric acid and igniting the nitrate.<sup>111</sup> According to von Bergkampff,<sup>58</sup> in precipitating gallium by means of cupferron the acidity should not be greater than that corresponding to 6 ml. of concentrated sulfuric acid in 400 ml. of solution. In tartaric acid solutions containing 20 ml. of sulfuric acid in 400 ml. of solution, iron and titanium are precipitated while gallium remains in solution. This makes possible a separation of iron and titanium from gallium.

The cupferron method is satisfactory for determining gallium by precipitating from hydrochloric or sulfuric acid solutions in the presence of aluminum, beryllium and indium.<sup>185</sup>

Moser and Brukl<sup>112</sup> have studied the precipitation of gallium with cupferron, and have suggested methods for the separation of gallium from aluminum, chromium, indium, uranium and cerium. The following method may be used for the separation of gallium from aluminum:

**Procedure.** To the neutral solution containing 0.01-0.3 g. of gallium, add sufficient sulfuric acid to make the final concentration 2 N and then dilute the mixture to 200-300 ml. At room temperature, add a 6 per cent solution of cupferron, using six times as much of the reagent as there is gallium present. Filter off the white flocculent precipitate through paper in a platinum cone and apply gentle suction. The first few ml. of the filtrate to come through is usually turbid, and this is treated with 1-2 ml. of the reagent and again passed through the same filter. If the filtrate remains clear for 2 hours, precipitation is complete. Wash the residue with small portions of 2 N sulfuric acid, and remove most of the liquid after each washing by applying gentle suction. Wash until free from chlorides, and then ignite and weigh as  $Ga_2O_3$ .

Gallium may be separated from chromium by the method described above. The separation of gallium from indium is the same as that described for the separation of gallium from aluminum except that special precaution must be taken in washing the gallium precipitate. A little cupferron must be added to the wash water, and if indium is present in the greater quantity, a double precipitation should be carried out. If the separation is incomplete and indium is present in the ignited gallium oxide, the residue will exhibit a yellow tint.

Gallium may be separated from hexavalent uranium by the same procedure. Precipitation must be carried out in the absence of reducing agents, since tetravalent uranium is precipitated with cupferron. Gallium may be separated from cerium by the same method.

Scherrer<sup>110</sup> has used cupferron for the determination of gallium in aluminum. Tin, copper, vanadium, titanium and zirconium are also precipitated, so the precipitate should be dissolved in 1.2 N hydrochloric acid and the resulting solution examined for the presence of these elements. If gallium alone is known to be present, gallium chloride is extracted by means of ether from a solution which is 6 N in hydrochloric acid. The volume of the acid solution should be 400 ml. prior to the extraction, and three extractions with 150 ml. of ether are sufficient. Gallium is eventually precipitated from the ether extract by means of cupferron.

Hoffman and Lundell<sup>54</sup> have used cupferron for the elimination of gallium in the preparation of pure samples of aluminum.

**Determination of tin.** When a 6 per cent aqueous solution of cupferron is added to an acid solution of stannic tin, an emulsion is formed which rapidly passes through a curdy condition, and with vigorous stirring changes into a stiff plastic mass. This finally becomes compact and brittle and may be crushed to powder with a glass rod. The complete series of transformations requires from about 30-45 minutes. The tin precipitate may be filtered during the curdy stage, but good results are also obtained if the mass has become hard and brittle. The precipitate is yellowish in color, and the solution clears noticeably upon the addition of an excess of the precipitant. After washing the precipitate with cold water, the filter and the precipitate are transferred to a weighed porcelain crucible, dried, carefully ignited, and finally weighed as  $\text{SnO}_2$ . If more than 0.3 g. of tin are precipitated and ignited, the resulting  $\text{SnO}_2$  has a tendency to retain some carbon, which is difficult to remove by ignition. This difficulty may be overcome by crushing the residue with a glass rod, and continuing the ignition. The results of a series of analysis using this method are given in Table 75.

TABLE 75.—THE DETERMINATION OF TIN AFTER PRECIPITATION WITH CUPFERRON

Tin Taken g.	Tin Found g.	Error mg.	Total Vol. ml.
0.1083	0.1087	+0.4	300
0.2068	0.2066	-0.2	170
0.1034	0.1032	-0.2	170
0.1216	0.1221	+0.5	400
0.2138	0.2142	+0.4	400
0.2068	0.2062	-0.6	500
0.1034	0.1036	+0.2	250

Stannic tin can be separated from trivalent antimony and arsenic and from lead, copper, cadmium and bismuth by precipitating all but the tin by means of hydrogen sulfide in the presence of 1-3 ml. of 48 per cent hydrofluoric acid per 100 ml. as described by McCay and Furman.<sup>113</sup> Fluoboric acid is formed by the addition of 2 g. of boric acid per 100 ml. of solution, and this makes

possible the use of a glass vessel in the analysis without danger of contamination by silica. Similar procedures can be used in the absence of hydrofluoric and boric acids, but are most valuable after the previous removal of the elements listed above, particularly lead, copper and antimony in babbitt and bearing metals or other tin-base alloys. Lead-base alloys, such as bearing and type metal, and zinc-base alloys such as aluminum solder or Woods metal, which contain aluminum and cadmium, may be analyzed for tin by the same procedure. Iron if present, generally only in traces, is precipitated along with tin when precipitating with cupferron. A satisfactory separation of tin from antimony, lead, copper and arsenic can be made in a solution containing 0.1-0.3 g. of tin and corresponding quantities of other cations in 500 ml. of solution containing 5 ml. of 48 per cent hydrofluoric acid, 4 g. of boric acid, 5 ml. of concentrated sulfuric acid, and 10 ml. of concentrated hydrochloric acid. Lead, antimony, copper and arsenic are precipitated from this solution upon the addition of hydrogen sulfide, but tin is not precipitated if present as the stannic ion. Tin is determined in the filtrate by precipitation with cupferron and ignition to  $\text{SnO}_2$ .<sup>113-115</sup>

The filtrate obtained by use of the McCay process for hydrogen sulfide separation has approximately the following composition: 0.1-0.3 g. of tin, 5 ml. of 48 per cent hydrofluoric acid, 4 g. of boric acid, 2-5 ml. of concentrated sulfuric acid and 5-10 ml. of concentrated hydrochloric acid in a total volume of 200-500 ml. Since it is from a solution of this composition that tin is ordinarily precipitated with cupferron, an analysis for tin with cupferron has been carried out in the presence of zinc (which would accompany tin into the filtrate in the McCay process) in this same medium. The results of such determination are shown in Table 76.

TABLE 76.—THE SEPARATION OF TIN FROM ZINC BY MEANS OF CUPFERRON

Tin Taken g.	Tin Found g.	Error mg.	Zinc Taken g.
0.1034	0.1037	+0.3	0.1479
0.2068	0.2069	+0.1	0.1479
0.1448	0.1444	-0.4	0.2958
0.1034	0.1040	+0.6	0.1479
0.1034	0.1032	-0.2	0.2958
0.2068	0.2073	+0.5	0.1479
0.1034	0.1037	+0.3	0.2958

Tin may be separated from manganese, cobalt and nickel under the same conditions without interference in the presence of 100-150 mg. of these elements. The separation is of about the same degree of accuracy as that shown in Table 76, which shows the separation of tin from zinc.

The method of Pinkus and Claessens<sup>114</sup> is excellent for determining 0.3-30 mg. of tin in the presence of 40-80 mg. of arsenic and antimony, provided the precipitation of tin with cupferron is carried out in the presence of a large

excess of reagent at a temperature of 3-5° C., and in a solution which is approximately N in hydrochloric acid.<sup>83</sup>

**Procedure.** Make the solution to be analyzed N in hydrochloric acid, cool to 3° C. with ice and dilute to 100-150 ml. Add with vigorous stirring a 5 per cent aqueous solution of cupferron. Continue to stir for 3 minutes after precipitation occurs, and finally add 15-20 ml. of the reagent in excess. Wash the precipitate by decanting 3 times with a cold 0.05 per cent cupferron solution, and finally on filter paper with water at room temperature. Dry at 60° C. and ignite carefully to  $\text{SnO}_2$ .

Mack and Hecht<sup>117</sup> have used cupferron for the separation of tin from antimony, and have carried out the precipitation in a hydrochloric acid solution containing tartaric acid. The following procedure for separating antimony and tin has been described by Gray:<sup>118</sup>

**Procedure.** Oxidize a solution containing stannous chloride and antimony chloride with hydrogen peroxide, and boil off the excess peroxide. Cool, and add a little more (not to exceed 5 per cent) than 2 times the theoretical quantity of cupferron solution, and then for every 100 ml. of the suspension of the tin precipitate, add 1 ml. of 1 per cent gelatin solution and a few drops of a 2 per cent tannin solution. Filter, wash, ignite, and weigh as  $\text{SnO}_2$ .

Clifford<sup>62</sup> has used cupferron for the elimination of iron and tin to avoid interference in the determination of lead in foods with the aid of dithizone. These elements along with about 80 per cent of the bismuth present, can be removed with cupferron without loss of lead.

Hoffman and Lundell<sup>54</sup> have used cupferron for the elimination of tin in the preparation of pure samples of aluminum.

Mogermann<sup>153</sup> has used cupferron for the determination of tin in non-ferrous metals after distillation as stannic bromide.

**Determination of columbium and tantalum.** Lundell and Knowles<sup>119</sup> have found that columbium and tantalum are completely precipitated with cupferron. According to Pied,<sup>120,121</sup> columbium and tantalum are quantitatively precipitated by the use of cupferron in solutions strongly acid with sulfuric acid and containing either tartaric or oxalic acid.

The columbium and tantalum determination is based on the following steps: Dissolve the freshly precipitated hydroxides of the metals in oxalic acid, add a little tartaric acid, and precipitate iron with ammonium sulfide. Allow to stand for some time, filter off the precipitate of iron sulfide, acidify the solution with sulfuric acid and expel hydrogen sulfide by boiling. Then add cupferron to the cold solution to precipitate tantalum and columbium. The appearance of white scum indicates complete precipitation. The precipitate should be filtered immediately with the aid of suction, and then dried and weighed.

The following procedure is described by Schoeller and Webb:<sup>122</sup>

**Procedure.** To 250-300 ml. of a solution containing 30 ml. of concentrated hydrochloric acid and 10 ml. of ammonium hydroxide, add the unknown

material and 3 g. of tartaric acid. At room temperature add an excess of cupferron, allow to stand for less than 1 hour, filter, wash with 10 per cent hydrochloric acid, ignite and weigh.

This procedure yields satisfactory results, but Schoeller and Webb<sup>122</sup> prefer the tannin method of precipitation.

Like tannin, cupferron does not precipitate tungsten alone, but a partial precipitation is induced by the presence of the so-called "earth acids." Tantalum and not columbium induces the more extensive tungsten precipitation, but columbium recovery is more complete than that of tantalum. The presence of tungsten causes considerable trouble in the analysis of tantalum and columbium.<sup>123</sup>

Since columbium and tantalum are precipitated from sulfuric acid solutions containing oxalic or tartaric acids, a separation is possible from aluminum, chromium and hexavalent uranium. By the use of oxalic acid, the rare earths can previously be separated from iron by means of the ammoniacal tartrate procedure described in preceding sections.

The following directions for the determination of columbium and tantalum in steel are taken from the work of Cunningham.<sup>124</sup> When titanium is present, proceed as follows:

**Procedure.** In the presence of more than 0.1 per cent titanium, determine columbium and tantalum by treating 2 g. of the steel with 20-30 ml. of 30 per cent hydrochloric acid at a temperature of approximately 80° C. When all action has practically ceased, add a few drops of hydrofluoric acid, and continue heating for several minutes longer. Cool the solution to about 15° C., dilute with cold water to 400 ml., and precipitate columbium, tantalum and titanium by the addition of an excess (20-30 ml. are usually sufficient) of a cold, freshly prepared, 6 per cent solution of cupferron. Add some ashless paper pulp, stir the solution vigorously for several minutes, and filter on two 11-cm., No. 42 Whatman filter papers containing some ashless paper pulp and supported on a Buchner funnel. Use gentle suction and wash the paper and precipitate at least 20 times with cold 10 per cent hydrochloric acid containing 20 ml. of cupferron solution per liter. Ignite the paper in a 100-ml. platinum dish at a low temperature, fuse with 3-5 g. of potassium pyrosulfate, and dissolve the melt, when cool, in 200 ml. of 5 per cent tartaric acid containing 4 ml. of 1:1 sulfuric acid. Then treat the solution with a brisk stream of hydrogen sulfide for 15-20 minutes. If a precipitate forms, filter on a 9-cm. paper containing some ashless paper pulp, wash 18-20 times with hydrogen sulfide water containing 0.5 per cent sulfuric acid and 5 per cent tartaric acid, and discard.

Add an excess of about 2 ml. of ammonia (d. 0.90) and treat the solution with hydrogen sulfide for 5 minutes longer. Add some ashless paper pulp, allow the precipitate of ferrous sulfide to digest at a temperature of approximately 70° C. for 10 minutes, and then filter. Wash well with ammonium sulfide water containing 2 per cent ammonium chloride and 2 per cent ammonium tartrate, and discard. Boil the filtrate to expel hydrogen sulfide, add 40 ml. of hydrochloric acid (d. 1.19), and continue the boiling until the volume is

reduced to about 300 ml. Cool the solution to 15° C., and then precipitate columbium, tantalum and titanium with cupferron and filter and wash as previously described. Ignite the precipitate, first at a low temperature, and finally at 1000-1050° C. Cool and weigh. Fuse the ignited and weighed precipitate with about 12 times its weight of potassium pyrosulfate, dissolve the melt in 100 ml. of 20 per cent sulfuric acid containing 1 g. of succinic acid and 1 ml. of 30 per cent hydrogen peroxide, and then determine titanium colorimetrically. Next add 25 ml. of a 20 per cent sulfuric acid solution containing 0.0500 g. of pure titanium dioxide (prepared by fusing the oxide with 2-3 g. of potassium pyrosulfate and dissolving the melt in the acid), and estimate the columbium in the solution by the procedure described below.

Determine columbium and tantalum in the absence of titanium as follows:

**Procedure.** Transfer 2-5 g. of the sample to a 600-ml. covered beaker, and treat with 25-50 ml. of hydrochloric acid (d. 1.19) and 10 ml. of nitric acid (d. 1.42) at a temperature of approximately 90° C. When all action has ceased, add 30-60 ml. of 60 per cent perchloric acid, boil the solution until dense fumes of perchloric acid are evolved, and continue the boiling for an additional 5 minutes to ensure the complete conversion of chromium to chromic acid. Add 200 ml. of hot water, 50-100 ml. of sulfurous acid, and 10 ml. of hydrochloric acid (d. 1.19), and boil the solution for 5 minutes. Add a fairly large quantity of ashless paper pulp, and allow the contents of the beaker to stand at a temperature of 60-70° C. for 15 minutes, or until the supernatant liquid is clear, and filter on an 11-cm. paper containing some ashless paper pulp. Scrub the beaker with a filter paper moistened with 2 per cent hydrochloric acid, and add to the filter. Wash the paper and precipitate 12-15 times with hot 2 per cent hydrochloric acid, and ignite in a 50-ml. platinum dish at a lower temperature to burn off the carbon of the filter paper.

Add approximately 5 ml. of 48 per cent hydrofluoric acid and 10 ml. of 1:1 sulfuric acid. Evaporate the solution to dense fumes of sulfur trioxide, and continue the evaporation until the volume is reduced to approximately 2.5 ml. to ensure the complete removal of all hydrofluoric acid. If the precipitate does not dissolve after heating for several minutes, add 2 ml. of 60 per cent perchloric acid and evaporate the solution as described above. If the evaporation is allowed to proceed almost to dryness, dissolve any separated columbic or tantalic acids by the addition of several ml. of sulfuric acid (d. 1.84) and heating for 1-2 minutes. Allow the contents of the dish to cool somewhat, and transfer to a 400-ml. beaker with the aid of about 200 ml. of hot 2 per cent hydrochloric acid. Remove any adhering precipitate from the dish by means of an 11-cm. filter paper moistened with hydrochloric acid, and add to the beaker. Add an excess (about 50 ml.) of sulfurous acid, and boil the solution 5 minutes. Add some ashless paper pulp, and digest the solution at a temperature of 60-70° C. for 15 minutes, or until the supernatant liquid is clear. Filter on an 11-cm. paper containing some ashless paper pulp, and wash 10 times with hot 2 per cent hydrochloric acid. Ignite the precipitate in a 50-ml. platinum dish, first at a low temperature to burn off the carbon of the filter paper, and finally to constant weight at 1000-1050° C. Cool and

weigh. For a control analysis, multiply the weight of the residue by 69.9 and divide the product by the weight of sample used. This gives the approximate per cent of columbium.

To the ignited and weighed precipitate of columbium and tantalum oxides, add 0.0500 g. of pure titanium oxide, and fuse the mixture with 2-3 g. of potassium pyrosulfate. Allow the dish and contents to cool somewhat, add 5 ml. of sulfuric acid (d. 1.84), and continue heating on a hot plate until a clear solution is obtained. Allow the contents of the dish to cool partially, transfer to a dry 250-ml. beaker, and rinse the dish successively with three 5-ml. portions of sulfuric acid (d. 1.84). Rinse the dish further with 20 ml. of 5 per cent succinic acid containing 1 ml. of 30 per cent hydrogen peroxide, and add the rinsings to the beaker. Stir the solution thoroughly, dilute to 100 ml. with cold water, heat to 60-70° C., and pass through a Jones reductor into a solution of ferric sulfate. Titrate with a standard solution of potassium permanganate. Columbium and titanium are reduced from  $\text{Cb}_2(\text{SO}_4)_5$  and  $\text{Ti}(\text{SO}_4)_2$  to  $\text{Cb}_2(\text{SO}_4)_3$  and  $\text{Ti}_2(\text{SO}_4)_3$ , respectively, while tantalum is not affected. The titanium added serves to prevent hydrolysis of the columbium and tantalum in the reductor. The columbous and titanous sulfates immediately react with the ferric sulfate to form  $\text{Cb}_2(\text{SO}_4)_5$  and  $\text{Ti}(\text{SO}_4)_2$ , respectively, and a corresponding amount of ferrous sulfate equivalent to the reduced columbium and titanium.

A Jones reductor having a column of 20-mesh zinc 75 cm. (30 inches) long is used. Amalgamate the zinc by treating 800 g. of the metal (low iron content) with 400 ml. of a 2.5 per cent mercuric chloride solution in an 800-ml. beaker and stirring vigorously for 2 minutes. Decant the solution and wash the zinc with water, and then transfer the metal to the reductor. Wash with hot 2.5 per cent sulfuric acid and water. The reductor, filled with amalgamated zinc as described, may be used for about 6 determinations, and then it should be emptied and filled with more zinc, freshly amalgamated.

Immediately before using the reductor, pass through it 200 ml. of almost boiling water to preheat the column of zinc. Then connect the reductor to a 1000-ml. suction flask with the delivery tube dipping beneath the surface of 25 ml. of ferric sulfate solution (prepared by dissolving 100 g. of ferric sulfate in a solution containing 150 ml. of phosphoric acid (d. 1.72), 20 ml. of 1:1 sulfuric acid, and 850 ml. of water). Now pass through the reductor the following solutions in the order named: the columbium solution, previously heated to 60-70° C.; 100 ml. of hot (60-70° C.) 20 per cent sulfuric acid containing 1 g. of succinic acid; and three 50-ml. portions of cold water. Do not permit the funnel which forms the reductor inlet to become entirely empty, and the reductor when not in use should be kept full of distilled water to cover the zinc metal.

Cool the solution to room temperature by the addition of several ice cubes prepared from distilled water, transfer to an 800-ml. beaker, and titrate with 0.05 N potassium permanganate that has been standardized against pure sodium oxalate. 1 ml. of 0.05 N potassium permanganate is equivalent to 0.002323 g. of columbium or 0.002395 g. of titanium.



Run a "blank" on the reagents and reductor by fusing a 0.0500-g. portion of pure titanium dioxide with 2-3 g. of potassium pyrosulfate (the same amount used in the analysis), dissolving the melt, and passing it through the Jones reductor, all as described in the above paragraphs. Cool the solution to room temperature and titrate with 0.05 N potassium permanganate. The total volume of standard 0.05 N potassium permanganate solution required, less the "blank" (including 0.0500 g. of titanium dioxide), is multiplied by 0.002323 and divided by the weight of sample taken to give the per cent of columbium. Multiply the weight of columbium found by 1.43 to give the corresponding weight of columbium pentoxide. The weight of the total oxides of columbium and tantalum, obtained as described above, less the weight of columbium pentoxide found, gives the weight of tantalum pentoxide, which, multiplied by 81.91 and divided by the weight of sample taken, gives the percentage of tantalum in the steel.

A modification of this method is necessary for steels containing molybdenum and tungsten. When titanium is present in amounts greater than 0.10 per cent, it is necessary to use the cupferron method described above.

**Detection and determination of bismuth.** Bismuth salts react with cupferron to form a precipitate which is practically insoluble in water or mineral acids of moderate concentration. This reaction has been used for the detection and determination of bismuth.<sup>125-127</sup> Bismuth is precipitated with an excess of the reagent in a hydrochloric or nitric acid solution, and the precipitate is ignited and weighed as  $\text{Bi}_2\text{O}_3$ . This procedure may be used in the presence of chlorides or sulfates. The separation of bismuth from sodium, potassium ammonium, cadmium, zinc, aluminum, arsenic, manganese, chromium, nickel, silver and lead is quantitative. All of these metals may be titrated by the usual methods in the filtrate and wash waters after removal of the excess cupferron. Lead and cadmium are also quantitatively precipitated by an excess of cupferron in a neutral solution. Ostroumov<sup>128,144</sup> has used the method of Pinkus and Dernies<sup>125</sup> for the determination of bismuth in the presence of lead and copper.

**Determination of aluminum.** Aluminum may be determined in the presence of sulfates, alkali metals, chromium, manganese, nickel, cobalt, zinc, and magnesium by precipitating with cupferron in an acid solution. The following procedure has been used by Pinkus and Belcke:<sup>129</sup>

**Procedure.** To 100 ml. of a solution containing 0.2 g. of aluminum and 0.005 N in acid, add dropwise a calculated 50 per cent excess of a 5 per cent solution of cupferron from a buret. If magnesium or heavy metals are present, wash the precipitate by decantation with 400 ml. of water containing a little cupferron, and then agitate for one hour or longer with 50 ml. of a 0.1 N hydrochloric acid solution containing 0.6 g. of cupferron per 100 ml. Filter and heat the precipitate in an electrically heated furnace while the temperature is slowly raised to a final heating of 35 minutes at 1000-1100° C.

This method is used for the separation of aluminum and magnesium.

Cupferron is used for the determination of aluminum in tungstic acid.<sup>180</sup> In this procedure, dissolve 10 g. of the sample in an excess of concentrated sodium carbonate solution, and precipitate the mixture with 8-hydroxyquinoline. After filtering, ignite the precipitate and fuse with pyrosulfate and leach with water. Acidify the solution and precipitate iron with cupferron. Filter and precipitate aluminum from the filtrate with cupferron by increasing the pH. To precipitate 0.1 mg. of aluminum, the volume of the filtrate should not exceed 100 ml. The aluminum precipitate is ignited and weighed or fused and determined colorimetrically with aluminon.

Meunier<sup>131</sup> and Schams<sup>141</sup> have used cupferron in a procedure for the determination of small quantities of aluminum in plants. The ash or dry plant material is dissolved in hydrochloric acid and the pH is adjusted to 2.5-4.5. This solution yields a precipitate with cupferron which on shaking with chloroform produces an opacity which can be measured for the estimation of aluminum. Results obtained by adding 0.01-0.06 mg. of aluminum to 1 g. of dry plant material showed an almost quantitative recovery of aluminum.

When cupferron is added to a neutral or faintly acid solution of an aluminum salt, containing less than 3 mg. of aluminum per liter, a colloidal solution is obtained which is yellow by transmitted light and bluish by reflected light. The formation of the colored compound may be used for the colorimetric or nephelometric determination of aluminum.<sup>132</sup>

This method is capable of giving results of average error less than 1 per cent and a maximum error of 3.2 per cent. Beer's law holds over a fairly wide range. The procedure differs somewhat according to the concentration of aluminum.

**Procedure. From 3-30 mg. of aluminum per liter:** To 25 ml. of the sample solution, add 1 ml. of a freshly prepared 5 per cent aqueous solution of cupferron and 1 ml. of a 0.1 per cent solution of gelatin. Treat a standard containing a known quantity of aluminum in the same manner, and compare in a colorimeter. The sensitivity is increased by interposing a piece of blue glass between the eye and ocular of the instrument.

**From 1.5-3 mg. of aluminum per liter:** Proceed as described above, but do not add the gelatin solution.

**From 0.15-1.5 mg. of aluminum per liter:** To 25 ml. of the sample solution, add 1 ml. of a freshly prepared 1 per cent aqueous solution of cupferron. Compare with a standard solution similarly treated, using a nephelometer with lateral illumination.

The standard aluminum solution is prepared by dissolving 0.2460 g. of aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , in 1 liter of 0.002 N sulfuric acid. This solution corresponds to 0.01 mg. of aluminum per ml. of solution.

This method is applicable in the presence of any substance not precipitated by cupferron in faintly acid solution if sufficiently dilute, such as antimonious, arsenious, arsenic, cadmium, chromium, cobalt, lead, magnesium, manganese, mercuric, nickel, silver and zinc salts. Chromic salts produce a turbidity at a chromium concentration of 5 mg. per ml. Copper, tin, antimonous, bismuth and iron interfere by forming slightly soluble compounds with cupferron.

Roquet<sup>180</sup> has described the following method for the determination of aluminum in steel:

**Procedure.** Transfer a sample of sufficient size to contain 50-100 $\gamma$  of aluminum to a platinum crucible and digest with 4-5 ml. of 7 N sulfuric acid. Add 3 g. of potassium bisulfate to the resulting solution, evaporate to dryness, and then fuse the residue. Cool, and heat the melt with 50 ml. of 3.3 N sulfuric acid. Cool and remove iron by electrolysis, using a mercury cathode. Filter the electrolyte, dilute to exactly 100 ml., and mix well. Transfer a 10- or 20-ml. aliquot to a second 100-ml. volumetric flask. Add 7 ml. of 20 per cent ammonium acetate solution, dilute to about 80 ml., and neutralize to pH 3.5, using bromophenol blue as indicator, by adding ammonium hydroxide or more acid as necessary. Add 1 ml. of a 5 per cent solution of cupferron, dilute to 100 ml. and note the time. In a photoelectric photometer, measure the opacity every 15 minutes at 15° or 23° C., and note the time required to give a constant opacity. The per cent aluminum in the sample is determined by reference to an empirical curve constructed from data obtained by treating samples of known aluminum content in a similar manner.

**Determination of mercury.** Mercurous salts in solutions containing less than 0.5 moles of free nitric acid per liter are precipitated quantitatively by cupferron.<sup>133</sup> Thus, mercurous ions can be separated from silver, lead, cadmium, aluminum, chromium, manganese, nickel, cobalt and zinc, provided the above acidity is maintained. Mercuric salts are only incompletely precipitated along with mercurous salts with cupferron. Quantities of mercurous ions ranging from 1-0.005 mg. per liter can be determined with an accuracy of 1-2 per cent by nephelometric methods.

**Determination of molybdenum.** The method for determining molybdenum which is based upon the color of colloidal molybdenum sulfide is not very satisfactory in the presence of high concentrations of salts. Bertrand<sup>184</sup> has improved this method by concentrating the molybdenum by forming a complex with cupferron and extracting with chloroform before applying the usual method for determining molybdenum colorimetrically.

**Determination of iridium.** Gilchrist<sup>185</sup> has recommended the use of cupferron for the precipitation of titanium in the determination of iridium in a mixture of the platinum metals.

**Microchemical reactions.** Martini<sup>186,187,142,145,187</sup> has used cupferron as a very sensitive reagent for the microchemical detection of uranium, cadmium, copper, barium, calcium and strontium.

Results obtained using these reactions are given in Table 77.

**Detection of tungsten.** Cupferron has been used to prevent interference of vanadium with the dithiol test for tungsten. Cupferron is used as the precipitant in the presence of hydrogen fluoride. Butyl acetate is used to remove the complex.<sup>146</sup>

TABLE 77.—MICROCHEMICAL REACTIONS WITH CUPFERRON

Metal	Sensitivity	Interference
Calcium .....	1:3000	Cu, Cd, U, Fe, Sr, Ba
Strontium .....	1:2000	Cu, Cd, U, Fe, Ca, Ba
Barium .....	1:1500	Cu, Cd, U, Ca, Sr

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## NEO-CUPFERRON

Synonym: Nitrosonaphthylhydroxylamine ammonium salt

$C_{10}H_{11}O_2N_3$

Mol. Wt. 205.19

$C_{10}H_7-N(NO)ONH_4$

**Use:** Determination of copper and iron.

Neo-cupferron can be prepared in a pure white form, but the filtered and washed product is found to have a light buff color. The compound dissolves in water with the formation of a faint yellowish colored solution, and upon standing the

solution turns reddish-brown and a precipitate forms. When heated to 125-126° C. neo-cupferron melts with decomposition.

**Preparation.** Neo-cupferron is prepared as follows:<sup>1</sup>

*$\alpha$ -Naphthyl hydroxylamine.* Dissolve 173 g. of  $\alpha$ -nitronaphthalene in 4325 ml. of 95 per cent ethyl alcohol in a 5-liter flask. Fit the flask with a 2-hole rubber stopper, and through one of the holes insert a glass tube having a bore of 10 mm. throughout its entire length except an adaptor extension 50 mm. in length and a 4 mm. bore through the hole in the stopper. The tube should reach to the bottom of the flask. Cool the flask and contents to 0° C. and saturate the mixture with anhydrous ammonia by passing a rapid stream of the gas through the solution. Then add a rapid stream of hydrogen sulfide gas until the flask is filled with yellow ammonium sulfide crystals. Finally, allow the flask and contents to stand with cooling for 24 hours, and pour the reaction mixture into a large volume of ice water. Filter off the white precipitate of  $\alpha$ -naphthylhydroxylamine, which is used for the next step in the synthesis.

*Neo-cupferron:* Weigh the moist product obtained in the above procedure, and dissolve in 1500 ml. of ether and transfer to a 2000-ml. separatory funnel and separate from the aqueous layer. Weigh the aqueous layer and subtract from the weight of the moist  $\alpha$ -naphthylhydroxylamine to determine the weight of the naphthylhydroxylamine used. Transfer the ether solution to a 2-liter flask which is immersed in ice, and which is fitted with a mechanical stirrer and a glass tube for admitting a stream of ammonia gas. The stopper closing the flask should also contain an additional hole for the addition of butyl nitrite. For each 100 g. of  $\alpha$ -naphthylhydroxylamine, add rapidly but dropwise 65 g. of butyl nitrite, while at the same time passing a rapid stream of ammonia gas into the flask, which is kept cold in an ice bath.

Filter the precipitate of neo-cupferron on a Buchner funnel and wash with ether. Dry on paper by spreading in thin layers and stirring frequently. The crude product is purified by dissolving in methyl alcohol and reprecipitating by the addition of ether. Filter and wash with ether and dry as before.

Solutions of neo-cupferron in water are not stable and should be prepared only as needed. The compound is sensitive to light and darkens upon exposure to daylight. The product is best stored in a bottle in which is suspended a little ammonium carbonate.

**Determination of iron and copper.** Neo-cupferron is similar to cupferron in its analytical reactions. It forms complexes with copper and iron which resemble those with cupferron (page 356).

Neo-cupferron was originally developed a number of years ago to make possible the determination of iron and copper in mineral water without previous concentration of the sample. The insolubility of the complexes of neo-cupferron with iron and copper, combined with the high molecular weight of these products causes the formation of a more voluminous precipitate and makes possible this application. The following procedure is used for the determination of iron:<sup>1</sup>



**Procedure.** To 25 ml. of the solution containing approximately 25 mg. of iron, add sufficient hydrochloric acid to make the normality of the acid 1.25 (1 volume concentrated hydrochloric acid and 9 volumes water), and then dilute to 200 ml. Cool to 10° C., add a little filter paper pulp, and add a cold 6 per cent aqueous solution of neo-cupferron. The excess precipitant can be determined by the appearance of a momentary flash of a white precipitate which forms at the contact of the precipitant with the solution containing the brown iron compound. Stir the precipitate for 3 minutes and filter on a coarse-grained, ashless paper. Wash with a cold 1 N hydrochloric acid solution containing a little of the precipitant. Allow the precipitate to drain as completely as possible, and then transfer the paper and contents to a weighed porcelain or platinum crucible. Char the filter and precipitate at a low temperature. Finally ignite at a bright red heat and weigh as  $\text{Fe}_2\text{O}_3$ .

Results using neo-cupferron are slightly higher than those obtained when cupferron is substituted for the former reagent in the above procedure. This may be caused by the greater solubility of the cupferron precipitate. This is indicated by the work of Bamberger and Baudisch.<sup>2</sup>

Most of the methods which have been proposed for the determination of iron in mineral water and sea water require the evaporation of large volumes of the sample. The evaporation is usually accompanied by the precipitation of considerable quantities of mineral salts, which may carry down a part of the iron contained in the sample. To avoid loss of iron from this cause, it is necessary to resort to a time-consuming separation of iron from the precipitate. By using neo-cupferron, however, both iron and copper can be precipitated directly from water without a preliminary concentration:<sup>1,3</sup>

**Procedure.** Acidify 400 ml. of the water to be analyzed with 25 ml. of concentrated hydrochloric acid and cool the mixture in ice water. Then add a cold, freshly prepared 1 per cent solution of neo-cupferron in 10-fold excess. Allow the mixture to stand in the cold for an hour, and then stir vigorously for 1 minute and filter. The use of a platinum cone and a slightly reduced pressure is recommended for the filtration. Wash the precipitate first with ice water, then once or twice with ice cold, 0.7 N hydrochloric acid and finally wash free of acid with ice water. Then dry the filter and contents at 105° C., and ignite in a platinum crucible to constant weight at the full heat of a Meeker burner with a free access of air. Weigh as  $\text{Fe}_2\text{O}_3$ .

With mineral waters containing copper, the latter is also precipitated quantitatively, and the mixture after ignition consists of  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$ . The quantity of copper is extremely small and may be separated from the iron and determined as follows:

Dissolve the ignited residue in hot hydrochloric acid, dilute with water, and precipitate with cupferron in the usual manner; a low acidity is required for the complete precipitation of copper. Wash the cupferron precipitate with ice water and then with ice cold 6 N ammonium hydroxide, which dissolves the copper quantitatively. Collect the ammoniacal filtrate in a platinum dish, evaporate to dryness and ignite. Dissolve the residue of copper oxide, and deter-

mine the copper colorimetrically. The most satisfactory procedure is based upon the production of the violet color of the copper complex obtained by precipitating an acid copper solution with zinc nitrate, mercuric chloride and ammonium thiocyanate.

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## CHAPTER XIV

### NITROSO AMINES

A study of aromatic amines reveals that compounds containing the *p*-nitroso-phenyl amino group,  $p\text{-NO—C}_6\text{H}_4\text{—N=}$ , such as *p*-nitrosoaniline, *p*-nitrosodimethylaniline,<sup>1</sup> *p*-nitrosodiethylaniline and *p*-nitrosodiphenylamine<sup>2</sup> form colored complexes with divalent palladium salts. These compounds are all of the same general type, and are typified by palladous dichlorodiammine,  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ .

Numerous amines yield complexes with palladous chloride but generally the product is yellow colored; thus, aniline<sup>3</sup> and *p*-nitroaniline<sup>4</sup> give yellow complexes with palladous chloride. In contrast, the palladium complexes of the above nitrosoamines are purplish-brown, dark-brown and bright red in color. Diethylaniline, dimethylaniline, *p*-aminophenol, *p*-chloroaniline and *p*-phenylenediamine do not give highly colored complexes with palladium salts. This appears to indicate that the nitroso group must be present to form highly colored complexes, and that the  $p\text{-NO—C}_6\text{H}_4\text{—N=}$  group is responsible for the characteristic reaction with palladium salts. The presence of the nitroso group is also responsible for more selective reactions for palladium. Thus diphenylamine and its amino or hydroxyl derivatives give highly colored reactions with numerous oxidizing agents, while the nitroso derivative reacts only with strong oxidizing agents. Similarly *p*-aminodiethylaniline reacts with weaker oxidizing agents than does *p*-nitrosodiethylaniline.

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#### *p*-NITROSOANILINE

Synonym: *p*-Quinoneimideoxime



Mol. Wt. 122.12

Beil. Ref. VII, 625.



**Use:** Detection and determination of palladium.

*p*-Nitrosoaniline crystallizes as steel-blue needles. It melts at 173-174° C. It dissolves readily in water with a formation of a green solution.

**Preparation:** Mix 1 part of nitrosophenol with 5 parts of ammonium chloride and 10 parts of dry ammonium acetate and digest the mass on a water-bath for one-half hour with the addition of a little ammonium carbonate. The mixture turns dark green and dark green crystals of *p*-nitrosoaniline separate on mixing with cold water. Extract the weakly ammoniacal solution with ether to recover more of the compound. To purify, dissolve in hot benzene, heat with animal charcoal, filter, cool and concentrate by evaporating until crystals appear.<sup>1</sup>

*p*-Nitrosoaniline contains the *p*-nitrosophenylamino group, and reacts as do other members of this class with palladium compounds to give a colored complex which can be used for the detection and determination of palladium. This reagent, however, does not appear to be as satisfactory as other compounds having similar structures which are described in this section.<sup>2</sup>

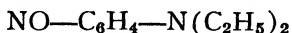
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### *p*-NITROSODIETHYLANILINE

$C_{10}H_{14}ON_2$

Mol. Wt. 178.23

Beil. Ref. XII, 684(338).



**Use:** Detection and determination of palladium.

*p*-Nitrosodiethylaniline is obtained as a green crystalline solid from ether or acetone. It melts at 84° C. It is only slightly soluble in water, but dissolves readily in alcohol and ether.

**Preparation:** Mix 50 parts of diethylaniline with 100 parts of concentrated hydrochloric acid and 600 parts of a mixture of 1 volume of hydrochloric acid and 2 volumes of alcohol. Cool with ice and mix with 75 parts of amyl nitrite at 0° C. Allow to stand for a few hours and shake the clear brownish-yellow liquid with ether to remove the amyl compound. Mix with an excess of sodium carbonate in aqueous solution, and again extract with ether. Add carefully to the ether extract a mixture of absolute alcohol and concentrated sulfuric acid to separate *p*-nitrosodiethylaniline sulfate as a yellow crystalline solid. Wash with an ether-alcohol mixture, dry, dissolve in a little water, and mix with a sodium carbonate solution. The free base separates as green crystals. Purify by recrystallizing from ether.<sup>1</sup>

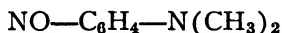
**Detection and determination of palladium.** *p*-Nitrosodiethylaniline, like other compounds of this group, forms a highly colored complex with palladium, which can be used for the detection or colorimetric determination of small quantities of this element. *p*-Nitrosodiethylaniline possesses the following advantages over *p*-nitrosodiphenylamine, which has been recommended for the determination of palladium (page 408): (a) a faster reaction rate; (b) a greater color stability; (c) a smaller temperature effect; and (d) it is more suitable for spectrophotometric studies. About five minutes are required for the development of the red color with palladium, and the solution is stable for about four hours. Since silver interferes with the determination of palladium chloride, palladium nitrate is determined in the presence of a nitric acid-sodium acetate buffer at a pH of about 4.7.<sup>2,3</sup>

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***p*-NITROSODIMETHYLANILINE** $C_8H_{10}ON_2$ 

Mol. Wt. 150.18

Beil. Ref. XII, 677(337).

**Use:** Detection of palladium.

Determination of hydrogen chloride, palladium and perchlorates.

*p*-Nitrosodimethylaniline is a green crystalline solid. It melts at 85° C. It is insoluble in water but dissolves in alcohol and ether.

**Preparation:** Dissolve 40 g. of dimethylaniline in 250 ml. of approximately 5 N hydrochloric acid. Immerse the vessel in ice and add 200 g. of ice. Then add to the well-stirred mixture a cold solution of 25 g. of sodium nitrite in 100 ml. of water. This solution should be run in from a separatory funnel at such rate that the temperature does not exceed 5° C. and no oxides of nitrogen are evolved. Allow the mixture to stand for 1 hour and filter the orange-yellow precipitate of *p*-nitrosodimethylaniline hydrochloride. Wash several times with 2 N hydrochloric acid and recrystallize from dilute hydrochloric acid. The solid is dissolved by warming, although the solution should not be boiled

The free base is prepared by rubbing the moistened salt under a sodium carbonate solution in a separatory funnel and shaking with ether until all has dissolved. Concentrate the emerald-green ether solution on a water-bath, and then allow the solvent to evaporate from a crystallizing dish.<sup>1</sup>

**Detection and determination of palladium.** *p*-Nitrosodimethylaniline reacts with a slightly acid solution of palladium chloride to yield a red precipitate or color. Since the color developed is proportional to the palladium content of the solution, this reaction may be used for the colorimetric determination of palladium.<sup>2,3</sup>

*p*-Nitrosodimethylaniline possesses the following advantages over *p*-nitrosodiphenylamine which has also been recommended for the determination of palladium (page 408): (a) faster reaction rate; (b) greater stability of color; (c) smaller temperature effect; and (d) it is more suitable for a spectrophotometric determination. The color develops within less than 5 minutes and is stable for about 4 hours. The reaction is sensitive to 1 part of palladium in 8 million parts of water.

The reagent cannot be used in solutions having a high neutral salt concentration. For example, the upper limit for sodium chloride is 0.05 M.

**Reagents.** *p*-Nitrosodimethylaniline: Dissolve 25 mg. of *p*-nitrosodimethylaniline in 50 ml. of 95 per cent ethyl alcohol and dilute to 100 ml. with water.

**Buffer solution:** Dilute a mixture of 80 ml. of 1 N hydrochloric acid and 200 ml. of 1 M sodium acetate with water to a total volume of 1 liter. The pH of this solution is about 4.8.

**Procedure.** The sample solution should be essentially free from neutral salts, and should be only slightly acid. Transfer an aliquot of this solution, containing not more than 10 $\gamma$  of palladium, to a 50-ml. volumetric flask. Add 10 ml. of the buffer solution and 0.5 ml. of the *p*-nitrosodimethylaniline solution, and then dilute to the mark with water and mix. Allow to stand 5 minutes and compare the resulting color with that obtained similarly with solutions containing known quantities of palladium.

Oxidizing agents, cyanide and iodide interfere. Tetravalent platinum does not react with the reagent, but except in small quantities it interferes because of its color. This is true also of the other platinum metals. Divalent platinum gives a sensitive color reaction with *p*-nitrosodimethylaniline which is similar to that of palladium. Gold reacts very much like palladium, but the reaction is much less sensitive. Silver interferes by precipitating as silver chloride. This interference may be eliminated by carrying out the determination with palladous nitrate, using a nitric acid-sodium acetate buffer of suitable pH.

**Determination of hydrogen chloride.** Vernon and Whitby<sup>4</sup> have recommended the use of *p*-nitrosodimethylaniline as an absorbent for hydrogen chloride gas. When hydrogen chloride is passed over *p*-nitrosodimethylaniline the gas is quantitatively absorbed. A valuable feature of this reaction is that it is additive. Carbon dioxide does not interfere. The marked color change from the deep green of the free base to the yellow of the hydrochloride is useful in indicating the exhaustion of the reagent.

The compound is quite stable and does not undergo change on exposure to air. *p*-Nitrosodimethylaniline is said to be much more satisfactory than partially dehydrated copper sulfate, which is frequently recommended.

**Determination of perchlorate.** Perchlorate may be determined by the violet color which is obtained in the reaction between perchlorates and *p*-nitrosodimethylaniline.<sup>5</sup> This reaction has been especially adapted to the determination of perchlorates in Chili saltpeter.

**Reagent.** *p*-Nitrosodimethylaniline solution: Dissolve 1 g. of *p*-nitrosodimethylaniline in alcohol and dilute to 1 liter.

**Standard perchlorate solution:** Dissolve 0.1393 g. of potassium perchlorate in water and dilute to 1 liter. Mix thoroughly and dilute 10 ml. of this solution to 100 ml. One ml. of the diluted solution contains 0.01 mg. of perchlorate.

**Procedure.** Dissolve the sample in 25 ml. of water and add 2 ml. of the *p*-nitrosodimethylaniline reagent. Mix well and allow to stand for several hours in a Nessler tube. Simultaneously prepare a series of standards by diluting measured quantities of the standard perchlorate solution to 25 ml. and adding 2 ml. of the *p*-nitrosodimethylaniline solution. Allow both standards and sample to stand for several hours and compare the resulting colors.

Iodides interfere with this determination but may be removed by treating with silver oxide. Iodates and periodates have no effect upon the reagent.

Yoe<sup>6</sup> reports that this method has been found to be valueless, and he does not recommend it for the determination of perchlorates.

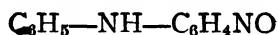
1. A. Baeyer and H. Caro, *Ber.* 7, 810, 963 (1874).
2. L. G. Overholser and J. H. Yoe, *J. Am. Chem. Soc.* 63, 3224-29 (1941); *C.A.* 36, 363 (1942).
3. L. G. Overholser and J. H. Yoe, *Va. J. Sci.* 1, 162-7 (1940).
4. W. H. J. Vernon and L. Whitby, *J. Soc. Chem. Ind.* 47, 255-8T (1928); *C.A.* 22, 4407 (1928).
5. A. Monnier, *Arch. sci. phys. nat.* 42, 210 (1916).
6. J. H. Yoe, *Photometric Chemical Analysis*, Vol. I, p. 164, John Wiley, New York.

***p*-NITROSODIPHENYLAMINE** Synonym: Phenylamino-*p*-nitrosobenzene

$C_{12}H_{10}ON_2$

Mol. Wt. 198.22

Beil. Ref. XII, 207 (294).



**Use:** Detection and determination of palladium.

*p*-Nitrosodiphenylamine is obtained as a green crystalline solid from benzene. It melts at 143° C. It is easily soluble in alcohol, ether and chloroform.

**Preparation:** Mix 30 g. of aniline, 30 g. of nitrobenzene and 120 g. of finely powdered, completely dry sodium hydroxide in a flask and heat in an oil-bath to 110-120° C. Stir frequently. After a short time the mixture is transformed into a thin liquid. If the temperature rises to 120-125° C. the liquid becomes darker and thicker. When the mass has solidified, the reaction is complete. Cool and dissolve in about 1 liter of hot water. Warm the mixture on a water-bath and allow to cool in an ice mixture until the base and azobenzene are crystallized. Filter with suction and wash several times with water to remove the alkali. Treat the strongly alkaline liquid with carbon dioxide and after about 2 hours filter off the bluish-black needles which separate. Treat the filtrate an additional 2 hours with carbon dioxide and collect a second crop of crystals. Add these to the first, and then purify by crystallizing from alcohol.<sup>1</sup>

**Detection and determination of palladium.** *p*-Nitrosodiphenylamine reacts with palladous chloride in a neutral or slightly acid solution to form either a deep red solution or a purplish-brown precipitate. As little as 0.005γ of palladium can be detected with this reagent by means of a spot plate test. The only other metallic ions which form colored compounds with this reagent are silver and gold, but the reactions with these metals are much less sensitive. Oxidizing agents interfere with the reaction, and cyanides and iodides prevent the formation of the colored compound. Precipitation is quantitative if an excess of the reagent is added to a slightly acid solution of a palladous salt. The compound appears to be  $Pd[C_6H_5NHC_6H_4NO]_2Cl_2$ .<sup>2-4</sup>

Small quantities of palladium may be determined colorimetrically by means of the color which appears when solutions of palladous salts are treated with *p*-nitrosodiphenylamine. *p*-Nitrosodiphenylamine appears to be superior to *p*-nitrosodimethylaniline for the palladium determination, since with the former a

higher concentration of iron, copper and gold is permissible. The reagent cannot be used in solutions containing high concentrations of neutral salts, since, for example, the determination fails if the concentration of sodium chloride exceeds 0.03 M. The following procedure may be used for the colorimetric determination of palladium in the presence of gold:<sup>3</sup>

**Reagents.** *p*-Nitrosodiphenylamine reagent: Dissolve 50 mg. of *p*-nitrosodiphenylamine in 500 ml. of 95 per cent ethyl alcohol and dilute to 1 liter.

**Buffer solution:** Add 240 ml. of 1 N hydrochloric acid to 200 ml. of 1 N sodium acetate solution and dilute to 1 liter.

**Procedure.** Add sufficient hydrochloric acid to 15 ml. or less of the palladium solution to make the concentration of the acid about 10 per cent. Transfer to a small separatory funnel, add 10 ml. of ethyl acetate or ethyl ether, shake, and drain off the acid solution. This treatment serves to remove most of the gold, which remains in the upper layer. Shake the ethyl acetate or ether layer with a little 10 per cent hydrochloric acid and again separate. If necessary repeat the treatment with ethyl acetate or ether. Evaporate the aqueous solution just to dryness, take up in a little hydrochloric acid and again evaporate nearly to dryness. Dissolve the residue in a little water, add 25 ml. of the buffer solution and 2 ml. of the reagent solution, and dilute to 100 ml. with water. Let stand 30 minutes and compare the resulting color with that obtained similarly with solutions containing known quantities of palladium, which should range from 0.5 to 50 $\gamma$ .

Since silver interferes with the determination of palladous chloride, palladous nitrate is determined in the presence of a nitric acid-sodium acetate buffer of pH 1.2.

**Reagent.** Dissolve 25 mg. of *p*-nitrosodiphenylamine in 50 ml. of ethyl alcohol and dilute to 100 ml. with water. Filter if any of the solid remains undissolved.

**Procedure.** Pipet 25 ml. of a sodium acetate-nitric acid buffer of pH 1.2 into a 100-ml. volumetric flask. Add the palladous nitrate solution, and 2 ml. of *p*-nitrosodiphenylamine reagent, and then dilute to the mark with water. Mix thoroughly and allow to stand for 20-30 minutes before making the color comparison. The color develops in about 30 minutes and is stable for 1-2 hours.

1. A. Wohl, *Ber.* **36**, 4135 (1903).
2. L. G. Overholser and J. H. Yoe, *J. Am. Chem. Soc.* **63**, 3224-29 (1941); *C.A.* **36**, 363 (1942).
3. J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.* **61**, 2058-63 (1939); *C.A.* **33**, 7691 (1939).
4. L. G. Overholser and J. H. Yoe, *Va. J. Sci.* **1**, 162-7 (1940).

### $\alpha$ -NITROSO- $\beta$ -NAPHTHYLAMINE

$C_{10}H_8ON_2$

Mol. Wt. 172.18

Beil. Ref. VII, 717.



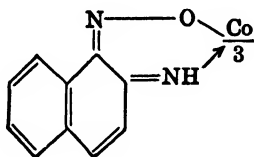
**Use:** Determination of cobalt, copper and nickel.



$\alpha$ -Nitroso- $\beta$ -naphthylamine is obtained in the form of green needles, which melt at 150-152° C. It is slightly soluble in hot water, and is easily soluble in most organic liquids.

**Preparation:** Mix 25 g. of  $\alpha$ -nitroso- $\beta$ -naphthol with 25 ml. of 10 per cent aqueous ammonia in a closed tube and heat for 10-15 minutes on a boiling water bath. On cooling the mass solidifies to a green paste. Filter with suction, wash with dilute ammonia and dissolve the raw material in dilute hydrochloric acid. Filter quickly and make the filtrate alkaline with ammonia. Filter, wash the crystals with water and crystallize from dilute alcohol.<sup>1,2</sup>

**Determination of cobalt, nickel and copper.** Cobalt is quantitatively precipitated as  $\text{Co}(\text{C}_{10}\text{H}_7\text{ON}_2)_3$ , by the addition of an alcoholic solution of  $\alpha$ -nitroso- $\beta$ -naphthylamine to a solution of a cobalt salt. This compound has been assigned the structure



This reaction may be used for the quantitative determination of cobalt.<sup>3</sup>

**Procedure.** To 300 ml. of a solution containing not more than 40 mg. of cobalt, add a slight excess of a 1 per cent alcoholic solution of  $\alpha$ -nitroso- $\beta$ -naphthylamine. Boil the mixture 20 minutes and allow to stand 15 minutes. Filter through a sintered glass filtering crucible and wash, first with dilute acid, then with a dilute base, and finally with hot water. Dry for 2 hours at 110° C. and weigh as  $\text{Co}(\text{C}_{10}\text{H}_7\text{ON}_2)_3$ . The factor for cobalt is 0.1030.

Excellent results are obtained in the presence of zinc, aluminum and chromium.

Dark salts of copper and nickel corresponding to  $\text{Cu}(\text{C}_{10}\text{H}_7\text{ON}_2)_2$  and  $\text{Ni}(\text{C}_{10}\text{H}_7\text{ON}_2)_2$  are obtained when an alcoholic solution of  $\alpha$ -nitroso- $\beta$ -naphthylamine is added to solutions of copper and nickel salts. Precipitation is quantitative and may be used for the determination of copper and nickel:

**Procedure.** To 300 ml. of a solution containing 15-50 mg. of copper, add 25 ml. of 10 per cent alkali tartrate solution, and heat to boiling. Add an excess of a 1 per cent alcoholic solution of  $\alpha$ -nitroso- $\beta$ -naphthylamine. Boil 20 minutes, allow to settle, and filter through a sintered glass filter crucible. Wash the precipitate with a little dilute alkali hydroxide solution, then with hot water, and finally dry at 105° C. and weigh. The factor for copper is 0.1566.

Nickel is determined by a similar procedure, but with nickel it is better to moisten the precipitate with nitric acid, and then heat and weigh as nickel oxide.

Good agreement is obtained in these determinations in the presence of cadmium, zinc, manganese, aluminum chromium and antimony.

1. M. Ilinski, *Ber.* 17, 391 (1884).
2. M. Ilinski, *Ber.* 19, 343 (1886).
3. S. S. Guha-Sircar, and S. C. Bhattacharjee, *J. Indian. Chem. Soc.* 18, 155-60, 161-3 (1941); *C.A.* 35, 7869 (1941).

### **$\beta$ -NITROSO- $\alpha$ -NAPHTHYLAMINE**

$C_{10}H_8ON_2$

Mol. Wt. 172.18

Beil. Ref. VII, 718.



**Use:** Determination of cobalt, copper and nickel.

$\beta$ -Nitroso- $\alpha$ -naphthylamine is a green crystalline solid. It is easily soluble in hot alcohol and benzene, but it is somewhat less soluble in ether and chloroform. It is only slightly soluble in hot water and is almost insoluble in cold water.

**Preparation.** Mix thoroughly 10 g. of  $\beta$ -nitroso- $\alpha$ -naphthol, 20 g. of ammonium chloride and 50 g. of ammonium acetate, and then heat on a water bath for 30 minutes. During this time stir the melt well and make strongly alkaline by careful addition of 20 g. of ammonium carbonate. The mass is red at first, and gradually darkens until it shows a greenish-luster. Cool, treat with cold water, filter and wash well with water. Crystallize the mass from 250 ml. of boiling benzene.<sup>1</sup>

**Determination of cobalt, copper and nickel.**  $\beta$ -Nitroso- $\alpha$ -naphthylamine is used in precisely the same manner as its isomer,  $\alpha$ -nitroso- $\beta$ -naphthylamine, for the quantitative precipitation of cobalt, copper and nickel. For the details of these procedures, see the above section.<sup>2</sup>

1. A. Harden, *Ann.* 255, 151 (1889).
2. S. S. Guha-Sircar and S. C. Bhattacharjee, *J. Indian Chem. Soc.* 18, 155-60, 161-3 (1941); *C.A.* 35, 7869 (1941).



# Part III

## ACIDIC IMINO COMPOUNDS



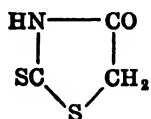
## CHAPTER XV

### RHODANINE AND ITS DERIVATIVES

In addition to oximes, nitroso, isonitroso, and nitro compounds, there are many other nitrogen-containing organic compounds which have acidic properties and are capable of forming analytically important salts with various metals. Since most of these compounds possess an active imino group, or a structure capable of producing an imino group by enolization, it may be assumed that salt formation results from the replacement of the imino hydrogen by an equivalent of a metal. It should be pointed out, however, that many compounds of this class have also either sulfur or oxygen atoms or both in the molecule, in addition to nitrogen, and the acidity may be due to any of the three. Consequently, the classification of compounds in this group must be somewhat arbitrary. The most important members of this class are the carbazides, carbazones, thiocarbazonones, and rhodanine and its derivatives.

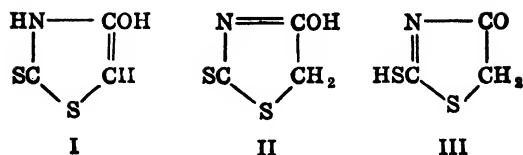
Many organic compounds having the NH group react in aqueous solution with cuprous, silver and mercury salts to form insoluble compounds. These substances are formed by the replacement of the imide hydrogen atom by an equivalent of the metal. Similar compounds with other metals are not common, and are never so simply prepared. The selective action of the imide group apparently is caused by the strong bond which develops between the silver, mercury or copper atom and the imide nitrogen atom. The strength of this bond is further emphasized by the fact that a number of the silver salts are insoluble in ammonia and acids. This property is often important in the solution of analytical problems.

Rhodanine,



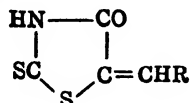
which forms a number of analytically important derivatives, yields yellowish-white precipitates with dilute nitric acid solutions of silver and mercury salts. The silver precipitate consists of the silver salt of rhodanine, while with mercury the sulfo salts are formed along with the simple mercury salt of rhodanine. Gold, palladium, platinum and cuprous salts also yield precipitates with rhodanine, although no other metals form similar compounds in nitric acid solution. Thus, in nitric acid solution rhodanine exhibits considerable selectivity in its reactions. In alkaline solutions, however, most metal salts yield precipitates with rhodanine, and these partially decompose to form sulfides.

The difference in the reactions of rhodanine in acid and alkaline solutions may be explained as due to a difference in structure resulting from enolization. The rhodanine molecule may give rise to three enol forms, I, II, III, by the tautomeric shift of one hydrogen atom.

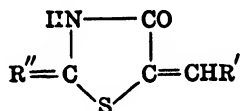


Therefore the ability of rhodanine to form a silver salt is due to the fact that in an acid solution there is 'little of the enol form, and only the silver-binding NH group is active, or that, even in acid solutions, the form containing the acidic hydroxyl or sulfhydryl group is present in sufficient quantity to permit the precipitation of the silver salt.

By altering the structure of the rhodanine molecule in such manner that certain enolic forms cannot exist, it is possible to determine the effect of various groups on the salt-forming properties of the original compound. For example, in rhodanine derivatives of the type

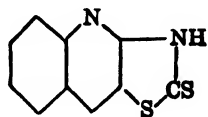


where R may be  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$  or  $\text{NOH}$ , enolization leading to compounds of type I is impossible. These derivatives, however, react like the keto form of rhodanine to yield insoluble silver salts, which indicates that the tautomeric form I is not essential for salt formation. Further, derivatives of the type



where  $\text{R}'$  may be  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$  or  $\text{NOH}$ , and  $\text{R}''$  may be  $=\text{N}-\text{NH}-\text{C}_6\text{H}_5$  or  $=\text{N}-\text{C}_6\text{H}_5$  also form salts with silver, thereby indicating that tautomeric forms I and III are not essential for salt formation.

Since the compound



also reacts like the keto forms of rhodanine, it is assumed that the enol form II is not essential for salt formation. A number of derivatives formed by condensing rhodanine with cyclic compounds, such as isatin, quinazolone and cyclohexanone, and with various sugars, such as glucose, retain their ability to form insoluble silver salts.

While the enol form III of rhodanine does not appear essential to the formation of an insoluble silver salt, this property is completely destroyed by replacing the sulfur atom in the thiocarbonyl group by oxygen or hydrogen. A similar replacement of the cyclic sulfur atom, however, does not similarly affect the

ability of the molecule to form an insoluble silver salt. Therefore, the group  $\text{—NH—CS—}$  appears to be responsible for the selective action of the rhodanine molecule.

By varying the structure of the molecule containing the silver-active group, it is often possible to confer upon it color-forming properties or solubility characteristics which result in an improvement in the analytical properties of the reagent. Among the important rhodanine derivatives which have been studied as analytical reagents are *o*-aminobenzalrhodanine, *o*-hydroxybenzalrhodanine, benzalrhodanine, isonitrosorhodanine, *p*-dimethylaminobenzalrhodanine and *p*-diethylaminobenzalrhodanine. These compounds are prepared by condensing aldehydes and ketones with rhodanine.

Tamchyna<sup>5</sup> has studied the sensitivity of the silver test, using as reagents compounds prepared by condensing various aldehydes and ketones with rhodanine. The reaction is carried out by acidifying 5 ml. of the solution to be tested with nitric acid, then adding 0.5 ml. of a 0.05 per cent alcoholic solution of the rhodanine derivative, and allowing to stand 3-5 minutes. Results are shown in Table 78.

TABLE 78.—SENSITIVITY OF SILVER TEST WITH RHODANINE DERIVATIVES

Compound Used	Aldehyde or Ketone Used	Limiting Concentration (appearance of turbidity)
$\text{C}_8\text{H}_8\text{ONS}_2$	.....	1:70-77,000
$\text{C}_8\text{HONS}_2=\text{CH—CHO}$	Acetaldehyde	1:100,000
$\text{C}_8\text{HONS}_2=(\text{CH}_3)_2$	Acetone	1:115,000
$\text{C}_8\text{HONS}_2=(\text{CH}_3)(\text{C}_2\text{H}_5)$	Methylethyl ketone	1:120,000
$\text{C}_8\text{HONS}_2=\text{CH—C}_6\text{H}_5$	Benzaldehyde	1:200,000
$\text{C}_8\text{HONS}_2=\text{CH—C}_6\text{H}_4\text{—CH}_3$	Tolualdehyde	1:200,000
$\text{C}_8\text{HONS}_2=\text{CH—C}_6\text{H}_4\text{O}_2\text{CH}_3$	Piperonal	1:200,000

1. Ch. Granacher, H. Reis and E. Pool, *Helv. Chim. Acta.* 5, 382-91 (1922); *C.A.* 14, 1667 (1920).
2. J. V. Dubsky, *Chem. Obzor.* 8, 71, 93 (1933).
3. F. Feigl, *Z. angew. Chem.* 39, 393 (1926).
4. F. Feigl, *Specific and Special Reactions*, pp. 110-114, Elsevier, New York (1940).
5. J. V. Tamchyna, *Mikrochemie* 9, 229 (1931).

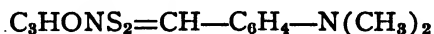
### *p*-DIMETHYLAMINOBENZALRHODANINE

Synonym: *p*-Dimethylaminobenzidinerhodanine

$\text{C}_{12}\text{H}_{12}\text{OS}_2\text{N}_2$

Mol. Wt. 264.35

Beil. Ref. XXVII, 433.



**Use:** Detection of copper, gold, mercury, palladium, platinum, and silver.

Determination of gold, mercury and silver.



*p*-Dimethylaminobenzalrhodanine is a red crystalline solid. It is variously stated to melt with decomposition between 200-246° C. and 240-270° C. It is insoluble in water, and is only slightly soluble in chloroform, ether, and benzene. It dissolves in strong acids with the formation of a yellow color.

**Preparation:** Dissolve equal molecular quantities of rhodanine (for preparation see page 428 and *p*-dimethylaminobenzaldehyde in acetic acid, and heat for 1 hour in a flask fitted with a reflux condenser. The condensation product may crystallize directly or it may be precipitated by the addition of water or alcohol. The product is purified by recrystallizing from boiling alcohol.<sup>1</sup>

**Detection of silver.** Rhodanine, and similar compounds which contain an active NH group, form insoluble silver salts in an acid solution. In these compounds the silver atom replaces the hydrogen of the cyclic NH group. The silver salt of *p*-dimethylaminobenzalrhodanine is red-violet in color, and is formed when an acetone solution of the reagent is added to a slightly acidified solution of a silver salt.<sup>2</sup> The reaction for the silver salt can be carried out only in an acid solution, since in an alkaline solution tautomeric changes take place in the rhodanine molecule which permits a color reaction or precipitation with practically all of the heavy metals. Further, some of these metals decompose the rhodanine group with the formation of a metallic sulfide. In acid solutions *p*-dimethylaminobenzalrhodanine also reacts with mercury, gold, platinum, palladium and cuprous salts, with which it forms insoluble compounds similar to that with silver.<sup>3-6,36-38</sup> Under controlled but comparatively simple conditions, however, the test for silver may be successfully carried out in the presence of salts of any or all of the above metals.<sup>7,8</sup>

In the absence of interfering ions, silver may be easily detected by means of a spot test or a test tube reaction.

**Procedure.** Impregnate a strip of filter paper with a saturated acetone solution of the reagent; and, when dry, add a drop of the slightly acid solution to be tested. A red-violet precipitate or stain is formed, depending upon the amount of silver present. The color is easily seen against the yellowish-brown background of the test paper. As little as 0.02γ of silver in 0.2 N nitric acid can be detected at a dilution of 1:2,500,000 by this method.

If the reaction is carried out in a test tube, it is best to extract the excess reagent with ether. In the presence of as little as 0.2γ of silver, violet flecks of the silver compound may be observed under the yellow ether layer.

Clarke and Hermance<sup>31</sup> claim that with a special spot technique as little as 0.004γ of silver may be detected.

The dimethylaminobenzalrhodanine test for silver is especially recommended by Wenger and co-workers.<sup>85</sup>

Since mercury salts also yield violet colored precipitates with *p*-dimethylaminobenzalrhodanine, these compounds interfere unless the conditions of the test are modified somewhat. The following procedure for silver is recommended in the presence of mercury salts:

**Procedure.** Place a drop of the solution to be tested on a spot plate, and add 1 drop of a 5 per cent solution of potassium cyanide to form  $\text{KAg}(\text{CN})_2$  and  $\text{Hg}(\text{CN})_2$ . Add a drop of a saturated acetone solution of the reagent, and a drop of 2 N nitric acid. The undissociated mercuric cyanide does not give a color reaction or precipitate with *p*-dimethylaminobenzalrhodanine, but the silver complex is sufficiently dissociated to give the characteristic silver color.

Hydrochloric acid or ammonium chloride may also be used in a modification of this test to convert the mercuric ion to undissociated mercuric chloride. The following procedure is used:

**Procedure.** Mix a drop of the solution to be tested on a spot plate or on a strip of filter paper with a drop of the reagent, and then add a few drops of dilute hydrochloric acid or ammonium chloride. The organic mercury compound dissolves, but the violet silver compound remains, since the silver rhodanine derivative is less soluble than silver chloride.

This method is particularly recommended when both copper and mercury salts are present, since cuprous cyanide which is formed with potassium cyanide is sufficiently dissociated to react with the reagent to give a violet cuprous salt, which resembles that of silver.

Silver may be detected in a mixture of the chlorides of silver, lead, and mercurous mercury, such as is formed in the systematic analysis of the cations, by first adding to the mixture a 5 per cent solution of potassium cyanide.<sup>24</sup> By this treatment,  $\text{KAg}(\text{CN})_2$ ,  $\text{Hg}(\text{CN})_2$  and metallic mercury are formed. After filtration, the silver in the filtrate is detected without interference by treating on a spot plate with a drop of an acetone solution of the reagent and 2 drops of 2 N nitric acid. The red color which appears in the presence of silver should be compared with that of a blank. By this method, 0.63% of silver may be detected in the presence of 1000 times as much lead chloride and mercury chloride. Davis<sup>32</sup> has also used this reagent for silver in a systematic scheme of analysis.

Gold, platinum, and palladium salts also react with *p*-dimethylaminobenzalrhodanine to give colored precipitates in acid solutions; but, in the absence of copper, silver can be detected in the presence of these substances by adding a little potassium cyanide, acidifying the reaction mixture with dilute nitric acid, and then adding the reagent. Under these conditions, silver reacts with the reagent, while gold, platinum, and palladium do not. The following procedure has been used by Feigl, Krumholz and Rajmann<sup>10</sup> for detecting silver in the presence of gold, platinum, palladium and mercury.

**Procedure.** Place 1 drop of the weakly acid solution to be tested on a spot plate, and mix with 1 drop of 10 per cent potassium cyanide. Add 1 drop of 0.03 per cent acetone or alcoholic solution of the reagent, and then add a few drops of 0.1 N nitric acid. A violet ring forms if silver is present.

By means of the above test 0.001 mg. of silver can be detected in the presence of 1000 times as much mercury, 4000 times as much gold, and 300 times as much palladium. Copper must be absent. Ettisch and Tamchyna<sup>11</sup> have

modified the silver test somewhat by applying the reagent to a suitable membrane containing adsorbed silver. By this method it is possible to detect 0.25 $\gamma$  of silver in 10 ml. of solution.

**Procedure.** The membrane is prepared as follows: Allow a thin film of an alcoholic solution of collodion to form on a glass plate. Immerse in water, which is frequently changed, and then loosen the film. Allow the membrane to remain 18 hours in an approximately normal solution of egg albumin or glycerol. Wash, and allow the membrane thus prepared to remain in 10 ml. of solution to be tested for 24 hours. Rinse with water and place in a test tube containing 0.5 ml. water and 1 drop of saturated solution of *p*-dimethylaminobenzalrhodanine. If silver is present the membrane appears reddish in color, but in the absence of silver it is distinctly yellow. The test may be made more sensitive by washing the membrane with acetone, which removes the yellow coloration which appears in the absence of silver.

Saturated solutions of silver chloride, silver thiocyanate, silver bromide and silver iodide give a yellow coloration with *p*-dimethylaminobenzalrhodanine; and, after standing for two days, a fine red crystalline precipitate is observed.<sup>12</sup>

Reith<sup>13</sup> has used *p*-dimethylaminobenzalrhodanine to detect silver in bismuth salts.

**Procedure.** To 0.02 g. of bismuth carbonate, add 2 ml. of 10 per cent hydrochloric acid, and after solution is complete add 2 ml. of 0.3 per cent acetone solution of *p*-dimethylaminobenzalrhodanine and 1.8 ml. of water. Mix well and add a few drops of water until a faint turbidity appears.

If silver is absent, the precipitate, which consists of bismuth oxychloride, BiOCl, and adsorbed reagent, is salmon colored, but if silver is present the precipitate is red or violet in color. The sensitivity of this reaction is 1:40,000. This test is reliable even in the presence of 0.01 g. of mercuric or cupric ions.

Miller<sup>14</sup> has studied a method for the analysis of the thallium group (system of Noyes and Bray) which consists of lead, silver, thallium and bismuth. In this scheme, silver is detected by means of *o*-dimethylaminobenzalrhodanine.

The *p*-dimethylbenzalrhodanine test for silver has been applied by Feigl and Ballaban<sup>15</sup> to the detection of silver in alloys, metal surfaces, jewelry, etc.

**Procedure.** Take a sample of the metal to be tested by carefully making a fine scratch on the surface of a piece of unglazed porcelain. Treat this with a very small quantity of nitric acid delivered from a fine capillary, and dry over a flame. While still warm, press the porcelain onto a strip of filter paper moistened with dilute nitric acid. Allow to stand for one minute, and treat with a few drops of the reagent. A red-violet streak appears on the paper if silver is present.

By carefully following the above procedure, silver can be detected in alloys and metals coatings without visible damage to the surface.

A number of special methods have been used to detect silver in various materials. Some of these are listed in Table 79.

TABLE 79.

Material	Reference No.
Assay beads .....	16
Minerals .....	17, 18
Opaque minerals .....	19
Wine or other fluids .....	20
Commercial lead .....	21

**Determination of silver.** Schoonover<sup>22</sup> recommends a procedure similar to that suggested by Feigl,<sup>2</sup> and later used by Kolthoff,<sup>5</sup> for the colorimetric determination of small quantities of silver.

**Procedure.** To 10 ml. of the solution to be analyzed add 0.5 ml. of approximately 4 N nitric acid and sufficient water to make the total volume 15 ml. Mix thoroughly and add 0.5 ml. of a 0.02 per cent alcoholic solution of *p*-dimethylaminobenzalrhodanine and again mix. Allow to stand for 30 minutes for the solution to attain a maximum depth of color. Compare the resulting color with that of a series of standards containing known quantities of pure silver nitrate. From 0.06-9.0 mg. of silver per liter may be determined by this method with an accuracy of 3 per cent.

In studying the conditions necessary for satisfactory results using this method, Schoonover found soft glass to be absolutely unsuitable. Jena glass is more satisfactory, but fused silica gives the best results. Appreciable quantities of silver are likely to be adsorbed by ordinary glass vessels, but the adsorption is negligible when silica ware is employed.

Yagoda<sup>23</sup> has used a semi-quantitative method for determining silver by means of a spot test with *p*-dimethylaminobenzalrhodanine.

**Detection of mercury.** Mercury salts yield a red-violet color or precipitate in neutral or weakly acid solutions with an alcoholic or acetone solution of *p*-dimethylaminobenzalrhodanine. This reaction may be used to detect mercury, either by a test tube or spot plate procedure.<sup>7,8,33</sup> The following method is used:

**Procedure.** Make the solution to be tested approximately 0.1 N with nitric or sulfuric acid, and place one drop of this mixture on a spot plate. Then add one drop of a saturated alcoholic solution of the reagent. A violet precipitate or a red color is formed, depending on the concentration of the mercury. The color of the reagent in an acid solution is colorless or faintly yellow, and consequently with low concentrations of mercury it may be necessary to run a blank with dilute nitric acid. As little as 0.33 $\gamma$  of mercury can be detected at a dilution of 1:150,000.

Large amounts of chlorides and of hydrochloric acid interfere with the formation of the mercury compound, since they reduce the ionization of the already weakly ionized mercuric chloride. In solutions buffered with acetates,

however, mercuric salts yield the red color with the reagent, even in the presence of an excess of chlorides. The following procedure may be used to detect mercury in the presence of chlorides:

**Procedure.** Make the solution to be tested about 0.1 N in nitric or sulfuric acid, and mix one drop of this solution on a spot plate with one drop of a saturated alcoholic solution of the reagent and a few drops of a saturated solution of sodium acetate. If mercury is present, a pink coloration appears. Since the reagent itself is colored yellow to orange on the addition of sodium acetate, a comparison test should be made on a solution containing a little nitric or hydrochloric acid. This reaction has about the same sensitivity as that in which chlorides are absent.

Under the conditions of the test described above, silver salts also interfere with the mercury test, and they must therefore be removed by precipitation with hydrochloric acid before making the test. Since by the above procedure the excess of hydrochloric acid is rendered harmless, this method is satisfactory.

Copper salts react with *p*-dimethylaminobenzalrhodanine in solutions that are neutral or strongly buffered with acetates to give a reddish coloration. Under suitable conditions, however, mercury can be detected in the presence of copper. When an acid solution containing a copper salt is treated with an excess of sodium phosphate, an insoluble light-green precipitate of copper phosphate is formed. The solubility of this compound is such that it gives no reaction with *p*-dimethylaminobenzalrhodanine. Due to the addition of the sodium phosphate, which is strongly alkaline, the acidity of the test solution is so reduced that the mercury gives a red color with the reagent. This color is visible even in the presence of the green copper phosphate.<sup>30</sup> The following procedure is used in the presence of copper:

**Procedure.** Make the solution to be tested about 0.1 N in nitric or sulfuric acid, and on a spot plate mix one drop of this solution with 5 drops of a 10 per cent sodium phosphate solution and one drop of a saturated alcoholic solution of *p*-dimethylaminobenzalrhodanine. A violet color forms in the presence of mercury. With low concentrations of mercury, it is best to make a blank test with dilute nitric acid for comparison. Using this procedure, 1γ of mercury can be detected in the presence of 450 times as much copper.

**Determination of mercury.** The red color which is formed when *p*-dimethylaminobenzalrhodanine is added to neutral or slightly acid solutions of mercury salts may be used for the colorimetric determination of mercury. Under carefully controlled conditions the intensity of the color produced is proportional to the amount of mercury present, but many factors affect intensity of the color.

The color may be developed in neutral or in acetic acid solutions, but in acid solutions the red color of the mercury compound is masked by the strong yellow color of the excess reagent. By adding a carefully controlled amount of nitric acid, the yellow color of the reagent is discharged, but the color due to the mercury compound remains. The mercury complex is formed by adding

*p*-dimethylaminobenzalrhodanine to a dilute solution of mercury of carefully adjusted acidity. An excess of nitric acid more or less completely prevents the formation of the mercury complex, and since the color of the reagent is just completely discharged in 0.1 N nitric acid, this acidity is not suitable for a satisfactory development of the color of the mercury compound. A reduction of acidity to 0.05 N gives a more certain and a more exactly reproducible red complex, particularly with quantities of mercury less than 0.05 mg. Under such conditions, however, the solution is faintly colored with the reagent, but this color is not sufficient to affect the sensitivity of the method. The solution must be thoroughly mixed to prevent an unequal concentration of the nitric acid. Best results are obtained when the concentration of mercury is 0.01-0.2 mg. in 100 ml. of solution.

The mercury complex is in the form of a colloidal dispersion, which eventually settles on standing, and for this reason the standards and the test solution must be prepared simultaneously.

Sulfates or halogens, even in traces, interfere. In the presence of chlorides, particularly hydrochloric acid, the intensity of the red coloration bears no relationship to the mercury content of the solution. Silver, cuprous, gold, platinum, and palladium salts interfere, but cupric salts do not.<sup>5,7,25</sup>

The following procedure, proposed by Strafford and Wyatt,<sup>25</sup> is used for the determination of from 0.01 to 0.2 mg. of mercury in 100 ml. of solution:

**Reagent.** Dissolve 0.04 g. of *p*-dimethylaminobenzalrhodanine in 200 ml. of ethyl alcohol, and allow to stand for 24 hours. Filter before using.

**Procedure.** Destroy any organic matter by careful heating with nitric acid, and dissolve a quantity of the sample containing about 0.1 g. of mercury in 5 ml. of 1.0 N nitric acid. Heat for 15 minutes on a water bath, cool, and transfer to a 100-ml. Nessler tube. Dilute the mixture to 95 ml., add 3 ml. of the reagent, and then dilute to the mark. Allow to stand for 5 minutes, and compare the resulting red color with that of standards similarly and simultaneously prepared. The standard mercury solution is prepared as follows: Dissolve 0.5 g. of clean, dry mercury in 5 ml. of nitric acid, dilute with 10 ml. of water, boil to remove the oxides of nitrogen, dilute with 250 ml. of water, boil again, and then dilute to 1000 ml.

The conditions using *p*-dimethylaminobenzalrhodanine as a reagent for the colorimetric determination of mercury are much less exacting than those with diphenylcarbazine, and the reaction is much more distinctive.<sup>25</sup>

**Detection of copper.** A 0.03 per cent alcoholic solution of *p*-dimethylaminobenzalrhodanine reacts with cuprous salts in neutral or slightly acid solutions to give a reddish-violet precipitate. Approximately 1 part of copper in 5 million parts of water can be detected by this reaction. A color reaction is also obtained with concentrated solutions of cupric salts, but the colored products are more soluble in water.<sup>5,26</sup> Cupric salts are reduced with sodium sulfite.

**Detection and determination of gold.** *p*-Dimethylaminobenzalrhodanine reacts with solutions of gold salts to yield a reddish-violet precipitate. After adding

the reagent to the solution to be tested, shake the mixture with ether, and observe the red layer which forms at the junction of the two liquids.<sup>10,16,27</sup>

The following procedure is described by Poluektov:<sup>34</sup>

**Reagent.** Mix 1 ml. of a 0.03 per cent alcoholic solution of dimethylaminobenzalrhodanine with 13 ml. of benzene and dilute to 50 ml. with chloroform.

**Procedure.** Acidify the solution to be tested with 3 drops of nitric acid, and add 0.5-1.0 ml. of the reagent. Shake vigorously. If gold is present, the color of the organic layer changes from yellow to a pink-violet. By comparison with a blank, 0.1-0.2 $\gamma$  of gold can be detected in 5 ml. of solution.

Poluektov<sup>34</sup> has used this reaction to determine gold in antimony.

Gutzeit<sup>28</sup> has applied the principle of dilution to the *p*-dimethylaminobenzalrhodanine-gold reaction for the approximate determination of gold in minerals. The method is based upon determining the limit of perception of the gold-*p*-dimethylaminobenzalrhodanine reaction, and then diluting a known volume of the sample under investigation until the test is barely visible. From the degree of dilution, the original concentration of the gold can be approximately determined. This method serves with as little as 0.02 $\gamma$  of gold.

Merejkovsky<sup>39</sup> used *p*-dimethylaminobenzalrhodanine for the determination of gold in biological samples. For the gold procedure, see section on diethylaminobenzalrhodanine.

**Detection of platinum, palladium and iridium.** Solutions of palladium salts react with *p*-dimethylaminobenzalrhodanine in neutral or weakly acid solutions to form a reddish-violet precipitate. This may be a palladium chloride addition product of the organic compound.<sup>6,9,10,27,29</sup> This reaction may be used for the detection of palladium.

**Procedure.** Place a drop of a neutral or acid solution to be tested on a strip of filter paper that has been impregnated with an alcoholic or acetone solution of *p*-dimethylaminobenzalrhodanine. If the test solution is neutral, a reddish-violet color appears if palladium is present. If the solution to be tested is acid, a blue-violet color appears with palladium.

This reaction is somewhat more sensitive in a neutral solution, than in an acid solution. In a neutral solution 0.004 $\gamma$  of palladium can be detected at a dilution of 1:12,500,000, while in an acid solution 0.006 $\gamma$  of palladium may be detected at a dilution of 1:8,000,000.

Both iridium and platinum salts react in an acid solution with *p*-dimethylaminobenzalrhodanine to give colorations which might be confused with that caused by palladium. Palladium may be detected in the presence of these two metals, however, since the platinum salts react only very slowly with the reagent to give a violet precipitate. When a drop of a solution of a platinum salt containing palladium is placed on the orange-yellow reagent paper, a violet circle or ring appears immediately in the middle of the spot, and this is surrounded by a moist ring. The central color is caused by the reaction between palladium and

the *p*-dimethylaminobenzalrhodanine. After about 1-2 minutes a red to reddish-violet color develops in the outer moist zone, due to the formation of the platinum compound. A 1:2,000 solution of platinic chloride containing palladium at a concentration of 1:2,000,000 gives a positive palladium reaction; thus 0.025 $\gamma$  of palladium can be detected in the presence of a thousand times as much platinum.

Iridium salts react in the same manner as palladium salts. This reaction is perceptible, however, only at a dilution of 1:20,000, and in view of the great dilutions common in the reaction with *p*-dimethylaminobenzalrhodanine, it appears likely that the reaction between the iridium compounds and the organic reagent may depend upon the presence of gold associated with the iridium. Osmium and ruthenium salts interfere with the palladium reaction, but only because of their color. As little as 0.025 $\gamma$  of palladium, at a dilution of 1:2,000,000, may be detected in the presence of 400 times as much osmium or 200 times as much ruthenium. 0.12 $\gamma$  of palladium at a concentration limit of 1:4,000,000 can be detected in the presence of 2000 times as much rhodium.<sup>10</sup>

Since both silver and palladium give similar color reactions with *p*-dimethylaminobenzalrhodanine, silver interferes with the detection of palladium. Palladium is determined in the presence of silver, however, if the latter is converted into a slightly dissociated complex ion,  $[\text{AgBr}_2]^-$ .<sup>10</sup>

**Procedure.** Place a drop of the neutral or slightly acid solution to be tested on a piece of filter paper that has been impregnated with an acetone or alcoholic solution of *p*-dimethylaminobenzalrhodanine and dried in air. After the drop has diffused through the paper, the violet spot is treated with a drop of saturated solution of potassium bromide. If palladium is present, the central region of the violet spot retains its color.

As little as 0.05 $\gamma$  of palladium at a dilution of 1:1,000,000 can be detected in the presence of 1000 times as much silver.

Gold also gives a reaction similar to that with palladium, and must be removed before making the palladium test. This is accomplished by reducing the gold salts in a neutral solution by heating with potassium nitrite.

By this treatment the gold salts are reduced to metallic gold, whereas palladium compounds are affected only very slightly.

**Procedure.** Place a drop of the acid test solution in a microcentrifuge tube, and add a very slight excess of precipitated calcium carbonate and a drop of potassium nitrite solution. Heat the mixture to boiling several times and separate the solid in the centrifuge. Using a capillary tube, transfer a drop of the clear solution to filter paper impregnated with the reagent. A violet color extending beyond the area of the original drop indicates the presence of palladium.

Using the above method, 0.1 $\gamma$  of palladium at a dilution of 1:500,000 may be detected in the presence of 5000 times as much gold.

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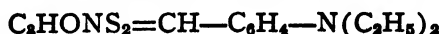
## **p-DIETHYLAMINO BENZALRHODANINE**

Synonym: *p*-Diethylaminobenzylidenerhodanine

$C_{14}H_{16}ON_2S_2$

Mol. Wt. 292.39

Beil. Ref. XXVII, 434.



**Use:** Determination of silver.

*p*-Diethylaminobenzalrhodanine is obtained as dark red needles from alcohol. It melts at 182° C.

**Preparation:** Mix equal molecular quantities of rhodanine and *p*-diethylaminobenzaldehyde, and heat for 1¼ hours in a flask in an oil bath. Dissolve the solidified melt in glacial acetic acid, and precipitate with water and a few drops of ammonia. Recrystallize from alcohol.<sup>1</sup>

**Determination of silver.** *p*-Diethylaminobenzalrhodanine reacts with silver to form a red-violet, slightly soluble product, which separates as a stable, very finely divided dispersion. This is suitable for the colorimetric determination of silver. With a silver concentration of 1 p.p.m. the maximum color develops almost immediately after adding the reagent, and is stable for about 30 minutes. With lower concentrations of silver, however, 15-20 minutes are required for maximum color development. Beer's law is valid over the concentration range of 0.1-1.0 p.p.m. of silver.

Palladium, gold, mercurous mercury, and cuprous copper must be absent, since they give highly colored products with the reagents. Lead and cupric copper in small quantities are practically without effect. Neutral salts may affect the color intensity.

The control of acidity in procedures using *p*-diethylaminobenzalrhodanine is very important. The acidity of the sample solution must be exactly the same as that of the comparison solution. A suitable acidity is 0.05 N. The sensitivity is strongly decreased in solutions of higher acidity.

The following method is recommended by Sandell:<sup>2</sup>

**Reagent.** Dissolve sufficient *p*-diethylaminobenzalrhodanine in alcohol to make a 0.05 per cent solution.

**Procedure.** Use 20 ml. of the sample solution, which is 0.05 N in nitric acid, and which has a silver content of 0.1-2.0 p.p.m. To this add 0.50 ml. of the reagent, dilute to 25 ml. and mix. Allow to stand 5 minutes if the silver concentration is approximately 1 p.p.m., or 20 minutes if 0.1-0.5 p.p.m., and then determine the transmittancy of the dispersion (green filter). Estimate the silver concentration by reference to a standard curve constructed from standards having precisely the same acidity as the sample solution, and containing the same concentration of foreign salts as the sample.

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## ISONITROSORHODANINE



Mol. Wt. 162.11



**Use:** Detection of mercury and silver.

Isonitrosorhodanine consists of yellow crystalline needles, melting at 151-53° C. The compound is readily soluble in alcohol.

**Preparation:** Pour 200 ml. of alcohol over 50 g. of rhodanine (see below) and treat this mixture with 50 ml. of a cold saturated solution of alcoholic hydrogen chloride. Place the mixture in a flask fitted with a reflux condenser and warm gently on a water bath, and with continuous shaking add amyl nitrite dropwise. The rhodanine is thus slowly dissolved. After 60 g. of amyl nitrite has been added, all the solid is dissolved except for a small quantity of impurities. Filter the reaction mixture, allow to cool, then cool with ice and neutralize with sodium hydroxide. Allow to stand in the cooling mixture until the compound separates as a yellow crystalline precipitate. Purify by recrystallizing twice from warm water.<sup>1</sup>

**Determination of silver and mercury.** Isonitrosorhodanine reacts with silver nitrate in a nitric acid solution to yield a yellowish-white precipitate of the silver derivative of isonitrosorhodanine. Mercurous and mercuric mercury also give precipitates with the reagent, but in the absence of mercury salt, the reaction is said to be specific for silver.<sup>2-5</sup> The sensitivity of the silver reaction is about the same as that of the silver chloride reaction. In the silver chloride precipitate, however, the percentage of silver is quite high (76.2 per cent), but in the isonitrosorhodanine precipitate it is much lower. The percentage error, therefore, is much less in precipitating silver with the organic reagent.

In the absence of silver, isonitrosorhodanine may also be used for the detection of mercury, although the mercury salt is less stable than the silver salt.

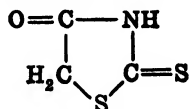
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## RHODANINE

$C_3H_3ONS_2$

Mol. Wt. 133.18

Beil. Ref. XXVII, 242.



**Use:** Detection and determination of silver.

Rhodanine is a pale yellow, crystalline solid which melts at 168-170° C. with decomposition. Only 2.25 g. of the reagent dissolves in 1 liter of cold water, although it is easily soluble in hot water, alcohol, ether, alkalis and ammonia.

**Preparation:** *Ammonium dithiocarbamate:* Pass the ammonia from 150 parts of ammonium chloride and 300 parts of calcium carbonate into 600 parts of

95 per cent ethyl alcohol, and add 96 parts of carbon disulfide. Crystallize at 30° C.<sup>12,18</sup>

**Rhodanine:** Dissolve chloroacetic acid in as little water as possible and neutralize with soda. Add an equivalent amount of ammonium dithiocarbamate ( $\text{CS}(\text{NH}_2)(\text{SNH}_4)$ ) and allow the mixture to stand 2 hours. Filter and acidify the filtrate with acetic acid. Upon standing for a day, rhodanine is almost quantitatively precipitated as a yellow crystalline solid.<sup>1,2</sup>

**Detection and determination of silver.** Rhodanine yields with silver salts an insoluble precipitate, which may be used for the detection and determination of silver.<sup>3-6,13</sup> Reith<sup>7</sup> has used rhodanine for the detection of silver in bismuth salts. Dubsky and others<sup>8-10</sup> have studied this reaction in connection with the relationship between the structure of the molecule and its salt forming properties.

Tamchyna<sup>13</sup> reports that the reaction is capable of detecting 65γ of silver at a dilution of 1:77,000.

Small quantities of silver may be determined as follows:

**Procedure.** Treat 3-4 ml. of a neutral solution of silver nitrate with 2-3 drops of 9 per cent nitric acid, and add an excess of a hot solution of rhodanine which was saturated when cold. Collect the yellowish-white crystalline precipitate of silver rhodanine in a Pregl filter tube, wash with cold 1 per cent nitric acid and then with alcohol, and finally dry with gentle heating in a current of dry air. Weigh as silver rhodanine. The precipitate contains 44.943 per cent silver.

The silver precipitate is more insoluble than silver chloride, and consequently the above method is more accurate for the microdetermination of silver than others which have been based upon the precipitation of the chloride.<sup>5</sup> Mercury is the only common element that interferes with this determination.

Kameyama and Makishima<sup>11</sup> have used rhodanine for the determination of small quantities of silver colorimetrically. With very small quantities of silver, a color is obtained which is said to be suitable for a colorimetric comparison.

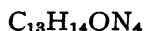
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## CHAPTER XVI

### CARBAZIDES, THIOCARBAZIDES AND SEMICARBAZIDES

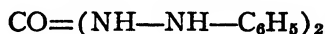
#### DIPHENYLCARBAZIDE

Synonym: Diphenylcarbohydrazide



Mol. Wt. 242.27

Beil. Ref. XV, 292.



**Use:** Detection of cadmium, chlorate, chloride, chromium, copper, hydrogen peroxide, iron, magnesium, mercury, molybdenum and periodate.

Determination of arsenic, chloride, chromium, iron, lead, mercury, molybdenum, phosphorus, sulfate and vanadium.

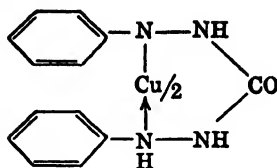
Diphenylcarbazide is a white crystalline solid which gradually turns pink on standing. It melts at 172-173° C. It is very slightly soluble in water, slightly soluble in hot alcohol, acetone, and glacial acetic acid.

**Preparation:** Dry 14 g. of powdered urea at 100° C. and mix with 40 g. of freshly distilled phenylhydrazine in a 250-ml. flask. Fit the flask with a reflux condenser, and heat in an oil bath at 155° C. for 2.5 hours. Remove the flask from the bath, and 3 minutes later add 250 ml. of 96 per cent alcohol to the yellow, oily contents. Transfer the reaction mixture to a 600-ml. beaker, and boil for 15 minutes until the solid is dissolved. Filter, and rapidly cool the alcoholic solution in a mixture of ice and salt. Filter off the crystals of diphenylcarbazide with suction and wash twice with ether, using suction, and then dry in air. The melting point of the crystals is 172° C.<sup>1</sup>

The following method may also be used:

**Preparation:** Mix 55 g. of guaiacol carbonate with 86 g. of phenylhydrazine and heat in an oil bath at 160-165° C. for two hours. Pour the mixture into an open dish, and cool slowly with stirring until crystallization begins. Stir to a paste and extract the guaiacol and the excess phenylhydrazine with benzene. Purify by recrystallization from hot alcohol. By this procedure only the symmetrical disphenylcarbazide is obtained.<sup>1</sup>

**Analytical reactions.** Diphenylcarbazide gives sensitive color reactions with many ions, particularly with those of the second group of the periodic system.<sup>2-5</sup> Some of the colored compounds are oxidation products, while others are chelate salts. Since diphenylcarbazide exists in two isomeric forms, two series of salts are possible, although the salts of the keto form are more valuable analytically than those of the enol form. Typical of the chelate salts is that of copper with the keto form of the reagent.



The colored products are extractable with immiscible organic solvents such as chloroform.

Among the more valuable color reactions with diphenylcarbazide are those with chromates, mercury, magnesium, silver, cadmium, molybdenum, copper, iron, lead, zinc, nickel, cobalt, and hydrogen peroxide in the presence of chromium.<sup>6,7</sup> These reactions have been summarized by Gutzeit<sup>8</sup> in Table 80.

TABLE 80.—COLOR OF VARIOUS METALLIC IONS WITH  
DIPHENYLCARBAZIDE

Metal	Color	Metal	Color
Mercury	Blue	Cobalt	Blue
Copper	Red	Manganese	Violet
Cadmium	Red	Magnesium	Violet
Silver	Violet	Zinc	Mauve
Lead	Pale rose	Iron (ic)	Blue-black
Nickel	Blue-violet		

**Detection of chromium.** Solutions of chromates in mineral acids react with diphenylcarbazide to give a soluble, violet compound of unknown composition. Since chromic salts can easily be converted to chromates by oxidation, diphenylcarbazide serves as a very sensitive reagent for chromium.<sup>9-16,73,74,76,77,85,101</sup>

**Reagent.** Dissolve 0.2 g. of diphenylcarbazide in 10 ml. of glacial acetic acid, and dilute with 100 ml. of 95 per cent alcohol.

**Procedure.** Make the solution containing the chromate acid with sulfuric acid, and add a few drops of the reagent. A reddish-violet color appears if chromate is present.

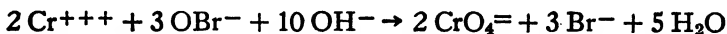
Since chromium often occurs in the form of chromic salts, oxidation to chromate is necessary before applying the above test. This may be accomplished in a variety of ways. A suitable oxidizing agent is an alkaline hypobromite solution, which may be used in the following manner:<sup>17</sup>

**Procedure.** Acidify the solution to be tested with mineral acid, and place 1 drop of this solution on a spot plate. Add a drop of saturated bromine water, and then 2-3 drops of 2 N potassium hydroxide. Mix thoroughly, test with litmus to make sure that the mixture is alkaline, and then add a drop of phenol. Finally, add a drop of diphenylcarbazide reagent, and then 2 N sulfuric

acid drop by drop until the red color of the alkaline diphenylcarbazide just disappears. In the presence of chromates a blue-violet color remains.

With this reaction 0.25  $\gamma$  of chromium can be detected at a dilution of 1:200,000.

The reaction between the chromic ions and the hypobromite takes place according to the following equation:



The excess bromine is removed by converting to tribromophenol with phenol.

Cobalt and manganese salts interfere in the above procedure, due to the precipitation of the hydrated oxides of cobalt and manganese. Nickel and copper salts also interfere, since their hydroxides are highly colored. By making a blank test, however, and allowing the precipitated compounds to settle, 1 $\gamma$  of chromium can be detected in the presence of 320 times as much cobalt, nickel, copper, and manganese.

Chromium may be oxidized to chromate in an acid solution by means of potassium persulfate, which is used in the following procedure:

**Procedure.** Mix a drop of the solution to be tested with a drop of a saturated solution of potassium persulfate and a drop of 2 per cent silver nitrate solution. Allow the mixture to stand 2-3 minutes, and add 1 drop of an alcoholic solution of diphenylcarbazide. If chromate is present, a violet to red color is formed. This fades on long standing.

As little as 0.8 $\gamma$  of chromium at a dilution of 1:625,000 gives a positive test.

Since silver ions are used to catalyze this reaction, large concentrations of halides must not be present. Under the conditions of the test, manganese compounds are oxidized to permanganates, and the violet color of the permanganate ion may mask the violet color of the chromate reaction. This difficulty is eliminated, however, by the addition of sodium azide, which completely reduces permanganates, but affects chromates only slightly.

Mercury salts, molybdates, and vanadates also yield blue to violet compounds with diphenylcarbazide, and as a result are likely to interfere with the chromate test. Interference due to mercury is prevented by converting the mercuric ion to slightly ionized mercuric chloride by the addition of an excess of an alkali chloride or hydrochloric acid. In testing for chromium in the presence of mercury, the alkaline solution of the chromate is acidified with hydrochloric acid. By this method, 0.25 $\gamma$  of chromium can be detected in the presence of 2.5 mg. of mercury.<sup>18</sup>

Interference due to molybdate is prevented by forming the molybdenum-oxalic acid complex,  $\text{H}_2[\text{MoO}_3(\text{C}_2\text{O}_4)]$ . The molybdate ion concentration in solutions of this complex is so low that the diphenylcarbazide reaction, or any other sensitive molybdate reaction, does not occur. The oxalic acid must be added to the solution to be tested before the diphenylcarbazide, since otherwise the molybdic acid is partially reduced to molybdenum blue by the reagent, and this compound is stable toward oxalic acid.<sup>18</sup>

**Procedure.** Mix 1 drop of chromate solution containing a maximum of 0.02 g. of  $\text{MoO}_3$  per ml. with 1 drop of saturated oxalic acid solution, and add 1 drop of 3 per cent alcoholic diphenylcarbazide, and a few drops of 2 N sulfuric acid. Chromate is indicated by the appearance of a violet color.

By the use of this procedure, 0.5% of  $\text{CrO}_3$  can be detected in the presence of 2,000 times as much  $\text{MoO}_3$ .

Thanheiser<sup>15</sup> has used diphenylcarbazide to detect chromium in steel. A drop of mineral acid is applied to the cleaned surface of the steel to be tested, and the drop so formed is transferred to a spot plate and tested according to the usual procedure. A similar procedure is used by Philbrook.<sup>85</sup>

**Reagents.** *Sodium hypobromite reagent:* Dissolve 5 g. of sodium hydroxide and 0.625 g. of sodium hypobromite in sufficient water to make 100 ml. of solution.

*Phenol solution:* Prepare a 5 per cent solution of phenol in 5 per cent acetic acid.

*Diphenylcarbazide reagent:* Dissolve 0.1 g. of diphenylcarbazide and 5 ml. of acetic acid in 50 ml. of ethyl alcohol.

**Procedure.** Place 1 drop of a mixture containing 40 per cent of concentrated nitric acid and 10 per cent phosphoric acid on the cleaned surface of the metal to be tested. When the reaction has subsided, remove the drop of liquid with a glass rod, and add to a little of the alkaline hypobromite solution. Add 1 drop of 20 per cent sulfuric acid to dissolve the precipitate and 1 drop of the phenol reagent. Finally add 1 drop of the diphenylcarbazide reagent. If chromium is present, a pale red color appears immediately.

Diphenylcarbazide has been used for the detection of chromium in several schemes of analysis.<sup>70-72</sup>

**Determination of chromium.** In acid solution diphenylcarbazide yields a soluble, red-violet product with hexavalent chromium. This reaction is extraordinarily sensitive, and is the basis for the best method yet devised for determining very small quantities of chromium. This method was first used by Moulin,<sup>19</sup> and has since been extensively studied.<sup>23-27</sup> The reaction is essentially specific, since the only other element giving a similar violet color is molybdenum, and this reaction is far less sensitive. Both mercuric and mercurous salts give blue or blue-violet colors, but these reactions are not sensitive except at low acidity. Ferric iron and pentavalent vanadium interfere by forming yellow or yellow-brown compounds with the reagent.

The acidity of the solution in which the chromium-diphenylcarbazide reaction is carried out should correspond to 0.2 N. In solutions of this acidity, the maximum color develops within a few seconds, while in solutions of lower acidity the color develops only after some time. An acidity greater than 0.2 N is undesirable, since under these conditions the color is less stable. In 0.2 N sulfuric acid the color is quite stable. This is shown in Table 81.



TABLE 81.—DETERMINATION OF CHROMIUM WITH DIPHENYLCARBAZIDE  
(Solution 0.2 N in sulfuric acid)

Cr Taken p.p.m.	Cr Found p.p.m.	Time After Mixing
0.405	0.413	2 mins.
0.405	0.410	10 mins.
0.405	0.403	20 mins.
0.405	0.388	2 hrs.

Sulfuric acid is recommended in preference to hydrochloric acid for acidifying the solution, since with the former acid, interference by iron is less likely to occur.

Beer's law is closely followed. Neutral salts are without effect on the color if present only in moderate quantity.

Although iron yields a yellow or brown color with diphenylcarbazide, chromium may be determined in the presence of a limited amount of iron. In a sulfuric acid solution, with chloride absent, the yellow color is weak, and good results are obtained by measuring the color immediately after adding the reagent. Approximately correct results are obtained in the presence of phosphoric acid by measuring the color immediately after adding the reagent. Further, by using a suitable green filter, interference by iron can be eliminated.<sup>23</sup> Iron usually causes little trouble in practical analysis, since it is generally separated in the oxidation of chromium.

Interference due to vanadium may be more serious, since it causes a stronger yellow color, and is not separated during the preparation of the sample for analysis. If the ratio of vanadium to chromium is not greater than 10:1, approximately correct results are obtained by allowing the mixture to stand 10 minutes after the addition of the reagent before measuring the color. The color caused by vanadium fades fairly rapidly, so that after 10-15 minutes an almost pure red-violet color due to chromium is obtained. Vanadium is best separated from chromium by converting to the hydroxyquinolate, and extracting with chloroform at pH 4.

The following procedure is recommended, since there is no interference from small amounts of mercury and molybdenum:<sup>91</sup>

**Reagents.** *Diphenylcarbazide:* Prepare a 0.25 per cent solution of the reagent in a 1:1 acetone-water mixture. A 0.25 per cent alcoholic solution may be used. The reagent should be prepared fresh each day.

*Sulfuric acid:* Free sulfuric acid of reducing substances by adding dilute potassium permanganate to the hot 6 N acid until a very faint pink color appears.

**Procedure.** To 10-20 ml. of the sample solution, which should contain 0.02-0.5 p.p.m. of hexavalent chromium, add sufficient sulfuric acid to make the concentration 0.2 N when diluted to 25 ml. with water. Determine the trans-

mittancy of the solution immediately after the addition of the reagent unless vanadium is present in appreciable quantity. In this case the color of the solution is red or brownish instead of red-violet. If vanadium is present the mixture should be permitted to stand 10-15 minutes before making the reading. Use a green filter having the transmission maximum at 540  $m\mu$ .

The determination may be made in a Duboscq colorimeter, and in this case the chromium concentration should be about 5 p.p.m.

Chromium may be determined in steel by the method of Agnew.<sup>20</sup>

**Procedure.** Dissolve about 1 g. of sample in 15 ml. of 9 N sulfuric acid and 20 ml. of water. Oxidize ferrous iron with 5 ml. of concentrated nitric acid, and boil the solution until free of the oxides of nitrogen. Dilute the solution to 200 ml. To 40 ml. of this solution, add 3 drops of saturated potassium permanganate solution and boil for 5 minutes and then add concentrated hydrochloric acid drop by drop (about 50 drops) to destroy the excess permanganate. At this point the solution should be clear. Cool, and add a slight excess of saturated sodium carbonate solution to precipitate iron. Dilute the mixture to 100 ml., and filter. To 50 ml. of the filtrate, add 20 ml. of 9 N sulfuric acid and 5 ml. of 0.1 per cent diphenylcarbazide solution. Compare the resulting color with that of a standard solution similarly treated and containing a known quantity of chromium.

The above method is particularly well suited for the determination of chromium in the presence of copper, nickel, molybdenum, vanadium, tungsten, and cobalt.

Evans<sup>101</sup> has used diphenylcarbazide for the determination of chromium in steel, and reports results accurate to within 0.0001 per cent for steels having a chromium content of 0.004-0.0017 per cent.

Loginov<sup>21</sup> and Gol'denberg<sup>22</sup> have used a similar reaction for the determination of chromium in air. Quantities of chromium as low as 0.07 mg. per liter may be determined with an accuracy of 6 per cent.

Miller<sup>2</sup> reports that diphenylcarbazide yields a characteristic color with solutions containing 1 part of chromium to 100,000,000 parts of solution, and has also applied this reaction to the determination of small quantities of chromium in dyestuffs or organic matter.

**Reagent.** Dissolve 0.2 g. of diphenylcarbazide in 10 ml. of acetic acid and dilute to 100 ml. with alcohol.

**Procedure.** Place 5 g. of the material to be analyzed in a Kjeldahl flask, cover with 25 ml. of concentrated sulfuric acid, and swirl the mixture until the solid is thoroughly wetted. Then add, a little at a time, 30 per cent hydrogen peroxide until the organic matter is completely destroyed. Boil the solution until heavy white fumes of sulfur trioxide appear, and then add cautiously a few ml. of nitric acid to remove the last traces of organic matter. Finally evaporate the mixture almost to dryness. Cool and add a slight excess of sodium hydroxide, and then 5-10 g. of sodium peroxide, and boil until the excess oxygen is removed. Filter if necessary and add dilute sulfuric acid to the filtrate until the mixture is just acid. Next add 2 ml. of the reagent solution and compare

the resulting color with that of standard solutions containing known quantities of chromate. The colors can be matched easily in any type of colorimeter.

The above method gives results which are accurate to within 5 per cent when less than 0.001 per cent of chromium is present.

Miller<sup>3</sup> has also proposed a method for determining small quantities of chromium in foodstuffs, cloth, leather and similar materials.

**Reagent.** Dissolve 0.2 g. of diphenylcarbazide in 10 ml. of acetic acid and dilute to 100 ml. with alcohol.

**Procedure.** Heat 10 g. of the material to be analyzed with 25 ml. of concentrated sulfuric acid until it is well charred, cool, and add cautiously 50 ml. of concentrated or preferably fuming nitric acid and heat until fumes of sulfur trioxide appear. Cool the mixture, and if the solution is turbid or dark, repeat the nitric acid treatment. Add 50 ml. of water and boil until oxides of nitrogen are completely expelled, and then pour the solution over about 75 g. of cracked ice. Neutralize the mixture with sodium hydroxide and add a little in excess, and boil with sodium peroxide until oxidation is complete. Make slightly acid with sulfuric acid, add 10 g. of sodium bisulfate, and boil the mixture until the excess peroxide is decomposed. Make certain that the solution is just acid. Add 10 ml. of 10 per cent sulfuric acid, and then add 2 ml. of the reagent solution. Stir vigorously and dilute to 100 ml. in a Nessler tube. Allow to stand for 10 minutes and compare the resulting red-violet color with that of standards prepared from a potassium chromate solution containing 0.1 mg. of  $\text{CrO}_3$  per ml. Add the standard solution from a buret to a blank of distilled water, sulfuric acid, and reagent until the color of the standard matches that of the blank or test portion. The per cent of chromium is calculated from the following equation:

$$\frac{\text{ml. standard chromate} \times 0.01}{\text{wt. sample}} = \text{per cent chromic oxide}$$

Diphenylcarbazide has also been used for the determination of chromium in a number of special materials, which are listed in Table 82.

**Detection of mercury.** Mercuric salts in an acid solution react with diphenylcarbazide to give a violet to blue precipitate of uncertain composition. The compound is probably a complex of the metal with diphenylcarbazide or its oxidation product, diphenylcarbazone. This reaction is used as a sensitive test for mercury.<sup>39-42,73,74,77,78</sup>

**Reagent.** Dissolve 2 g. of diphenylcarbazide in 10 ml. of acetic acid and 10 ml. of alcohol.

**Procedure.** Add a few drops of the reagent to a little of the solution to be tested and shake, and then add a little 10 per cent sodium acetate solution. A blue color forms with mercuric ions.<sup>43,44</sup>

A sensitive spot reaction has been proposed by Feigl and Neuber.<sup>45</sup>

TABLE 82.

Material	Reference
Silicate rocks .....	28
Minerals and rocks .....	29, 86
Steel .....	20, 30, 36, 101
Cast iron and steel .....	31
Wrought iron .....	32
Air .....	33
Plant ash, soil, water, and rocks .....	34
Toxicological studies .....	35
Titanium oxide .....	37
Fats .....	38
Tumors .....	87, 88
Dyes .....	102
Foods, cloth and leather .....	103

**Procedure.** Impregnate filter paper with a freshly prepared 1 per cent alcoholic solution of diphenylcarbazide and treat this with a drop of the solution to be tested. With 0.001 mg. of mercury, a violet spot is obtained. This becomes darker on exposure to ammonia.

According to Miller,<sup>102,103</sup> a deep violet color is obtained when a saturated alcoholic solution of diphenylcarbazide is added to a chloride-free solution of a mercury salt that has been buffered to pH 3.6-4.0. If the pH is properly controlled, 1 part of mercury can be detected in 1,000,000 parts of solution.

Lead, bismuth, and a little copper do not interfere with the mercury test, although large quantities of copper and cadmium are objectionable. Mercury can be separated from these metals by precipitation as the sulfides with hydrogen sulfide, followed by treatment of the precipitate with nitric acid.

Chromates and molybdates give color reactions which are similar to that obtained with mercury, but interference due to chromate is easily prevented by reducing with hydrogen peroxide or sulfurous acid to chromic ions. Molybdates are converted to the complex molybdenum-oxalic acid compound, which does not react with the reagent. The presence of chlorides affects the test due to the formation of molecular mercuric chloride.

The colored compound produced when diphenylcarbazide reacts with mercuric ions dissolves in benzene, but the corresponding mercurous compound is insoluble. If, therefore, a solution of a mercury salt is treated with a benzene solution of diphenylcarbazide, the benzene is colored only if mercuric compounds are present, and a colored product is formed at the junction of the two liquids if a mercurous salt is present.

**Determination of mercury.** The colorimetric determination of mercury by measuring the purple color produced when mercury compounds react with diphenylcarbazide is suitable for quantities of mercury ranging down to 0.8 mg. per liter, but special precautions are necessary to obtain satisfactory results.<sup>46,79</sup> As reagent, use a freshly prepared solution of diphenylcarbazide in absolute

alcohol. The solution to be analyzed must not be more than 0.003 N in electrolyte, must contain no chloride, and should have a pH of 3.5-4.5. Further, for a given series of comparisons, the acidity must not vary more than 0.3 pH unit.<sup>47</sup>

The color disappears in a few hours in sunlight with the formation of a precipitate, but it is stable for several days if kept in the dark. If the solution containing the mercury is weakly acid, a cold saturated solution of sodium acetate should be added. The determination cannot be made in strongly acid or alkaline solutions. Zinc, iron, cobalt, nickel, lead, copper, silver, gold, cyanides, bromides, and iodides interfere.<sup>48</sup>

A comparison of the methods employing diphenylcarbazide and diphenylcarbazone indicates that the latter reagent is the more satisfactory, because conditions necessary for its use are less exacting than those using diphenylcarbazide.<sup>49</sup> Further, diphenylcarbazone may be obtained in greater purity, and consequently gives a more uniform color reaction.<sup>50</sup>

Böttger<sup>51</sup> has proposed the following method for the determination of mercury:

**Procedure.** To the mercury solution to be analyzed, add a 1 per cent alcoholic solution of diphenylcarbazide, a little petroleum ether, and some aluminum sulfate. Collect the blue-violet precipitate which forms at the junction of the two liquids on an asbestos filter, decompose by the Carius method in a small tube, and recover the mercury by electrolytic deposition.

Böttger<sup>51</sup> has also used a spectrophotometric method.

Diphenylcarbazide has been used as an indicator for titrating mercuric ions with a halide. Mercuric ions react with the reagent to give a blue-violet coloration, and in this manner the end point of the reaction between mercuric and halide (chloride) ions to form molecular mercuric chloride can be determined accurately.<sup>52,53</sup>

**Detection of cadmium.** When an alcoholic solution of diphenylcarbazide is added to a neutral or acetate solution of a cadmium salt, a red-violet precipitate or coloration is formed depending on the concentration of the cadmium salt.<sup>80,81</sup> The colored compound appears to be the cadmium salt of the reagent.

A sensitive spot test for cadmium is carried out as follows:<sup>45</sup>

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper that has been impregnated with an alcoholic solution of diphenylcarbazide and allowed to dry. Hold over an open bottle of ammonium hydroxide for 1-2 minutes. A blue-violet coloration appears if cadmium is present. As little as 4γ of cadmium at a dilution of 1:12,500 can be detected by this method.

This reaction is not specific for cadmium, but by modifying the above procedure, cadmium can be detected in the presence of small quantities of copper, mercury, and lead. Cadmium is detected in the presence of copper after the latter has been reduced to the cuprous state, since cuprous salts do not give a precipitate with diphenylcarbazide.

**Procedure.** To prepare the test paper, soak filter paper in a cold, saturated solution of diphenylcarbazide in 90 per cent alcohol which has been saturated with potassium thiocyanate, and to which a few crystals of potassium iodide have been added. This reagent is spotted with a drop of the solution to be tested. In the presence of cadmium, a blue-violet coloration appears. Copper does not interfere.

With this procedure, 8 $\gamma$  of cadmium can be detected in the presence of 273 times as much copper.

In a test tube reaction for cadmium, lead does not interfere, but as a spot reaction on filter paper a coloration appears with lead which might be mistaken for that with cadmium. By using the following procedure, however, 8 $\gamma$  of cadmium can be detected by a spot reaction in the presence of 80 times as much lead:

**Procedure.** As the reagent, use the paper prepared above for detecting cadmium in the presence of copper. When a drop of the solution containing both cadmium and lead is placed on this paper, lead iodide is formed at the center, while the cadmium diffuses outward to form a colored zone around the margin of the spot.

Mercury and bismuth do not interfere with this test, provided the concentration of the metals is not too great.

Cadmium salts yield a bright violet color when treated with diphenylcarbazide in the presence of ammonium thiocyanate and potassium iodide. A reagent for the detection of cadmium is prepared by saturating a saturated solution of diphenylcarbazide in alcohol with ammonium thiocyanate and potassium iodide. When this reagent is added to a nearly neutral solution of a cadmium salt, and this is followed by a slight excess of ammonia, a bright violet color is obtained with 1 part of cadmium in 100,000 parts of solution.

**Detection of copper.** Copper is detected by the following procedure:

**Procedure.** Add a few drops of a freshly prepared 1 per cent alcoholic solution of diphenylcarbazide to a few drops of a neutral solution to be tested. An intense violet color appears with 1 part of copper in 1000 parts of solution.

With more dilute solutions, shake 5 ml. of a cold solution of the reagent in benzene with 10 ml. of the solution to be tested. Solutions having a dilution of 1:100,000, which show no color with potassium ferrocyanide, give a distinct reaction.<sup>73,74</sup>

**Detection and determination of iron.** Ferric salts give a red coloration with a benzene solution of diphenylcarbazide. The reaction is perceptible at a dilution of 1:100,000,<sup>73-75</sup> and may be used for the detection of iron.

Diphenylcarbazide is also used as an indicator for the titration of ferrous iron with potassium dichromate.<sup>69</sup>

**Determination of lead.** A very pale pink color is formed when an acetone solution of diphenylcarbazide is added to a solution of lead nitrate con-

taining pyridine nitrate. On standing this color deepens slowly, and reaches a maximum after 20 hours. The intensity of this color is proportional to the quantity of lead present.<sup>54</sup> This reaction has been used for the colorimetric determination of small quantities of lead.

**Reagent.** Mix 120 ml. of purified pyridine with 2 ml. of 6 N nitric acid, and add this solution to 10 ml. of a 1.5 per cent solution of diphenylcarbazide in alcohol. Allow the mixture to stand overnight before using. This solution keeps fairly well for several days, but in time it deteriorates, and finally fails to give a color reaction with lead.

**Procedure.** Treat 100 ml. of the neutral solution to be analyzed, which contains about 2 mg. of lead nitrate, with 10 ml. of the above reagent, and compare the resulting dark, cherry-red color with that of a blank, which is a pale, orange-blue color.

The addition of acetone causes the color formed in the above reaction to deepen, but very dilute nitric acid causes it to disappear. The addition of a little ammonia causes the color to become darker, but with more ammonia the color disappears.

Any substance which precipitates lead under the conditions of the test, such as arsenate, phosphate, vanadate, tungstate, molybdate, and citrate destroys the color immediately.

Excellent results are obtained by titrating a lead solution with standard phosphoric acid solution, using diphenylcarbazide reagent (for preparation see above) as the indicator. Metavanadic acid, molybdic acid, phosphoric acid, and arsenic acid can be titrated by measuring the volume of lead nitrate solution required to give an end point with the diphenylcarbazide reagent.

Lead may also be determined satisfactorily by precipitating as the chromate, and then determining the amount of chromate present in the precipitate with diphenylcarbazide.<sup>55,56,82</sup>

Results reported for this method have not been altogether satisfactory. The method is theoretically sound, but requires refinement as to detail.<sup>89</sup> It is said to require more time and to be less accurate than the titration of the resulting dichromate solution after liberation of the equivalent quantity of iodine.<sup>90</sup>

**Procedure.** Wet-ash the sample containing 0.01-0.2 mg. of lead, and dilute the solution of the ash to 250 ml. Make the solution just alkaline to methyl orange by adding 25 per cent sodium hydroxide solution, and then make just acid with 1:2 hydrochloric acid. The solution should be clear at this point. Dilute to 300 ml. and saturate with hydrogen sulfide. Pass the hydrogen sulfide into the solutions for 1 hour with thorough mixing. Allow the solution to stand overnight, and filter through an 11-cm. filter paper. Transfer the precipitate to the paper with hot water. Wash with 5 ml. of a mixture of 3 volumes of strong ammonium sulfide solution and 2 volumes of 1:1 ammonium hydroxide, and then wash the filter thoroughly with hot water. Discard the filtrate and washings. Dissolve the lead sulfide from the filter with 5 ml. of hot 1:1 nitric acid, added in several portions. Collect the solution in a 250-ml. beaker. Wash the vessel

in which the sulfide was precipitated with an additional 5 ml. of 1:1 nitric acid, and pour this through the filter. Wash the vessel once with hot water, and then wash the filter with hot water until free of acid.

Boil the acid solution to remove all hydrogen sulfide, and then cool. Add a drop of phenolphthalein, and make the solution alkaline by the careful addition of 25 per cent sodium hydroxide solution. Add 2 ml. of 50 per cent acetic acid and 5 ml. of 0.1 N potassium dichromate and mix well. Cover the beaker with a watch glass and boil for 2 minutes. Allow to stand at least 3 hours at room temperature, and filter on a small paper. Wash the beaker and filter thoroughly with hot water to remove all soluble chromates. Discard the filtrate and washings. Carefully rinse the beaker in which the chromate was precipitated, and in this collect the filtrate obtained by pouring 25 ml. of 1:20 hydrochloric acid over the precipitate on the paper. Pour a second 25-ml. portion of the acid through the paper, and then wash the paper thoroughly with cold water. Collect the solution and washings in a 250-ml. volumetric flask. Add 2 ml. of a 1 per cent solution of diphenylcarbazide in glacial acetic acid. Dilute to volume and mix thoroughly. Compare the resulting pink color with standards prepared from a solution containing 0.0142 g. of potassium dichromate per liter. One ml. of this solution is equivalent to 0.02 mg. of lead. A somewhat similar method is carried out as follows:

**Reagents.** *Diphenylcarbazide reagent:* Dissolve 0.4 g. of diphenylcarbazide in 10 g. of glacial acetic acid.

*Standard dichromate solution:* Dissolve 0.1420 g. of pure potassium dichromate in water and dilute to 1 liter. One ml. of this solution is equivalent to 0.2 mg. of lead.

**Procedure.** Precipitate lead from the material to be analyzed as lead sulfide and wash the precipitate with 5 per cent sodium sulfide solution. Dissolve in boiling, dilute nitric acid and evaporate to dryness. Heat the residue to 130-150° C. for 1 hour and allow to cool. Dissolve the residue in 10 ml. of water and again evaporate to dryness. Cool, dissolve the residue in 5 ml. of water and add a crystal of sodium acetate.

Add the neutral lead solution to 25 ml. of the standard potassium dichromate solution, and then add 0.1 g. of pure, finely divided asbestos and shake for 10 minutes. Filter, and dilute the filtrate to 100 ml. with washings. Mix the combined filtrate and washings, and test a 5-ml. portion for an excess of dichromate by adding 2 drops of 6 N nitric acid and 1 drop of diphenylcarbazide reagent. A violet color indicates that an excess of dichromate was used. If an excess is not indicated, evaporate the filtrate to dryness, and add it to a second 25-ml. portion of the standard dichromate solution. Again test for excess dichromate and repeat until an excess is present. Finally determine the excess dichromate by comparing the violet colored solution with that obtained by treating a measured quantity of standard dichromate similarly with diphenylcarbazide reagent. The quantity of lead present is estimated from the quantity of dichromate precipitated.



Kehoe and co-workers<sup>58</sup> have used diphenylcarbazide for the determination of lead in urine and feces. Jones<sup>57</sup> has proposed the use of diphenylcarbazide for determining lead in non-ferrous alloys, and Letonoff,<sup>58</sup> and Letonoff and Reinhold<sup>59</sup> have used a similar method for determining lead in blood, tissues, and excreta.

**Detection of magnesium.** Both magnesium hydroxide and magnesium carbonate are colored a deep red by heating with an alcoholic, alkaline solution of diphenylcarbazide. The color is stable, and is not affected by boiling with water. This coloration is probably due to the formation of an adsorption compound of the magnesium hydroxide or carbonate and the reagent. A simple test for magnesium is carried out simply by adding a solution of the reagent in alcohol and potassium hydroxide to the solution to be tested. An insoluble red precipitate indicates the presence of magnesium. Since many other ions yield colored products, the reaction is not specific.<sup>60</sup> Feigl has used diphenylcarbazide to detect magnesium in rocks and minerals.<sup>61,62,75</sup>

**Procedure.** Magnesium ammonium phosphate, obtained in the usual scheme of analysis, is moistened while on the filter paper with a hot alcoholic solution of diphenylcarbazide containing potassium hydroxide, and is then washed with hot water until a colorless filtrate is obtained. If magnesium is present in the precipitate, a reddish-violet solid will remain on the paper, but if the precipitate does not contain magnesium, it remains white with this treatment.

Silicates are treated with hydrogen fluoride, and the resulting solution is heated with an alkaline, alcoholic solution of diphenylcarbazide. If magnesium is present, a bluish-violet color is obtained.<sup>63</sup>

Magnesite and dolomite are differentiated by a method proposed by Feigl and Leitmeier.<sup>64</sup>

**Reagent.** Place 1-2 g. of diphenylcarbazide in a test tube half-filled with alcohol, warm until solution is complete, and then add 3 ml. of 25 per cent sodium or potassium hydroxide solution.

**Procedure.** Pour 5 ml. of the reagent over a particle of the solid mineral to be tested, boil for 2-3 minutes, decant the liquid, and boil water over the solid until the supernatant liquid remains colorless. Magnesite so treated is colored reddish-violet, while dolomite remains uncolored.

**Detection of molybdenum.** Lecocq<sup>65</sup> used diphenylcarbazide for the detection of molybdenum. An indigo-violet color appears when an alcoholic solution of the reagent is added to a solution of ammonium or sodium molybdate which has been acidified with hydrochloric acid. Excess acid or alkali interferes by preventing the formation of the color.

The following test has been proposed by Korenman and Frum:<sup>84</sup>

**Procedure.** Acidify 3 ml. of the solution to be tested with 1 ml. of concentrated hydrochloric acid, and add an excess of crystalline sodium sulfite. Shake and add 5 drops of a saturated alcoholic solution of diphenylcarbazide and

1 ml. of ether. A pink or red color appears in the ether layer if molybdate is present. This method is sensitive to 0.05 mg. of molybdenum in 3 ml. of solution.

**Detection of hydrogen peroxide.** The familiar test for hydrogen peroxide, which depends upon the formation of blue, ether-soluble perchromic acid, can be made more sensitive with the aid of diphenylcarbazide. This reagent reacts with perchromic acid to form a reddish-violet color, which appears in the ether layer even though the blue color of the perchromic acid is scarcely visible.<sup>66</sup>

**Procedure.** Make the solution to be tested acid with 2-3 drops of 20 per cent sulfuric acid by volume, and then add 3-4 ml. of freshly prepared absolute ether, and a few drops of 0.01 N potassium dichromate. Shake, and cautiously add to the separated ether layer 2 drops of diphenylcarbazide solution. This is prepared by heating a few crystals of diphenylcarbazide with 0.5 ml. of 96 per cent alcohol, and then adding, when cold, 5 ml. of absolute ether. As little as 5γ of hydrogen peroxide in 5-10 ml. of liquid can be detected.

Reducing agents, such as ferrous iron, sulfite, and alcohols interfere with the above test, and must be destroyed by the addition of bromine. The excess bromine must be removed by the addition of phenol, because of its color and its ability to oxidize diphenylcarbazide.<sup>67</sup>

**Procedure.** Acidify the solution to be tested with several drops of dilute sulfuric acid, and add bromine water until a stable yellow color appears. To 2-3 ml. of this solution, add 2 ml. of chromate solution, and, after 5-6 minutes, several drops of phenol. When the solution is decolorized, add 2-3 drops of diphenylcarbazide reagent, and proceed with the test in the usual manner.

The reaction of diphenylcarbazide with perchromic acid can be used for the colorimetric determination of hydrogen peroxide, and also as a spot test for peroxides.

**Determination of sulfate.** When a solution of a sulfate reacts with barium chromate, barium sulfate is precipitated, and an equivalent quantity of soluble chromate is left in solution. After removing the excess barium chromate by treating the mixture with calcium hydroxide, the quantity of soluble chromate in the solution may be determined by the color which it forms with diphenylcarbazide. This principle has been used for the determination of sulfur in serum and urine.<sup>68,92</sup> By this method, a quantity of sulfate equal to only 0.1 that which can be estimated by benzidine is readily determined.

Phosphates react like sulfates and must be removed. Since urine contains substances capable of reducing chromates, a preliminary treatment is necessary to avoid incorrect results. Iron also interferes, but with more than 0.17 mg. of iron per ml. of final solution this interference may be eliminated by adding 1 ml. of 20 per cent hydrochloric acid to the solution before adding diphenylcarbazide. By so adjusting the quantity of barium chromate used that from 20 to 80 per cent of it reacts with the sulfate, the method is capable of an accuracy to within 2 per cent of the true value.

The following method is used for the determination of free sulfate in urine<sup>96,97</sup>

**Reagents.** *Barium chromate solution:* Dissolve 24.4 g. of barium chloride in water and heat to boiling. Dissolve 14.7 g. of potassium dichromate in another portion of water, and heat this solution to boiling. Mix the hot solutions and filter the precipitate of barium chromate. Boil the precipitate several times with 1 per cent acetic acid, and then wash with water until the washings give only a trace of color with the diphenylcarbazide reagent. Dry at 110° C. Dissolve 1.2670 g. of the dried barium chromate in 100 ml. of 1 N hydrochloric acid and dilute to 1 liter. This solution is 0.01 N.

*Diphenylcarbazide reagent:* Dissolve 2 g. of diphenylcarbazide in 10 ml. of glacial acetic acid and dilute to 100 ml. with 96 per cent alcohol.

**Procedure.** Add 0.5 g. of calcium hydroxide to 10 ml. of urine and shake well. Centrifuge, and to 2 ml. of the centrifugate, add 5-10 drops of 30 per cent hydrogen peroxide and 1 drop of 1 per cent ferric chloride solution. Boil for 10 minutes, and add 0.05 g. of manganese dioxide to destroy the excess hydrogen peroxide. Add 1-2 drops of 1 N sodium hydroxide and filter. To 1 ml. of the filtrate, add 9 ml. of the barium chromate reagent and mix thoroughly. Add 0.5 g. of calcium hydroxide, mix, and allow to stand 5 minutes. Centrifuge, and dilute 1 ml. of the centrifugate to 10 ml. with water. Add 1 ml. of the diphenylcarbazide reagent, mix, allow to stand 20 minutes, and compare with a standard. The standard is prepared by adding 0.5 ml. of the 0.01 N barium chromate solution to 10.5 ml. of water. One ml. of the barium chromate solution is equivalent to 0.1603 mg. of sulfur, 0.4803 mg. of sulfate and 0.4904 mg. of sulfuric acid.

**Determination of chloride.** When silver chromate is added to a solution containing a soluble chloride, silver chloride is precipitated, and an equivalent quantity of chromate passes into solution. The colorimetric estimation of the soluble chromate provides an indirect determination of the amount of chloride originally present in the solution. This principle has been used by Leton-off<sup>98,99,100</sup> for the determination of small quantities of chlorides in biological fluids.

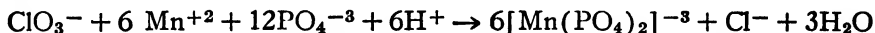
**Reagents.** *Diphenylcarbazide solution:* Add 0.1 g. of diphenylcarbazide to 500 ml. of ammonia-free distilled water and heat to boiling. Cool, dilute to 500 ml. and store in a brown bottle. This solution is stable for 1 month.

*Standard sodium chloride solution:* Dissolve 0.5 g. of pure sodium chloride in water and dilute to exactly 2 liters. 0.1 ml. of this solution contains 0.025 mg. of sodium chloride.

**Procedure.** Transfer exactly 1.9 ml. of water to a centrifuge tube, and add 0.1 ml. of blood, plasma, cerebrospinal fluid, or serum, and rinse the pipet with water. Add 0.05 g. of zinc borate, stopper the tube, and shake for 30 seconds. Allow to stand for 2 minutes and filter through a small paper. Wash

the precipitate well, and combine the filtrate and washings. To this add an excess of silver chromate and mix well. Centrifuge, filter, and wash, and combine the filtrate and washings. Dilute to a suitable volume, and to 0.2 ml. of this solution add 3 ml. of 10 per cent acetic acid, and 10 ml. of the diphenylcarbazine reagent. Mix and allow to stand 10 minutes. Compare the resulting color with that of a standard similarly and simultaneously prepared. The standard should contain 1 ml. of the standard sodium chloride solution.

**Detection of chloric acid.** In a solution containing phosphoric acid, chlorates react with manganous sulfate when heated to form a complex trivalent manganese phosphate ion.



This ion has a violet color similar to that of the permanganate ion. This reaction has been used by Feigl<sup>94</sup> as a means of detecting chlorates. If the color of the solution of the complex manganese ion is very faint, it may be intensified by the addition of a little diphenylcarbazine. This causes a more definite violet coloration, due to the formation of an oxidation product of diphenylcarbazine.

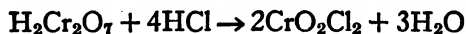
**Reagent.** Mix equal volumes of a saturated solution of manganese sulfate and syrupy phosphoric acid.

**Procedure.** Mix a drop of the solution to be tested with a drop of the reagent in a small porcelain dish. Warm rapidly and allow to cool. A violet color appears if chlorate is present. If the color is very faint, add a drop of a 1 per cent alcoholic solution of diphenylcarbazine. The violet color is intensified if chlorate is present. As little as 0.05% of chlorate can be detected at a concentration limit of 1:1,000,000.

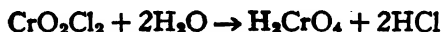
Persulfates and periodates give similar reactions. Persulfates may be destroyed by evaporating the sulfuric acid solution with a little silver nitrate, but the test cannot be applied in the presence of periodates.

**Detection of periodate.** Periodates react with manganous sulfate on heating with concentrated phosphoric acid to form the same violet complex manganese phosphate ion which is produced in the reaction with chlorates. The test is carried out in the same manner as for chlorates.<sup>95</sup> As little as 5% of periodate can be detected at a concentration limit of 1:10,000.

**Detection of chloride.** When a solid chloride (excepting silver chloride and mercurous chloride) is treated with concentrated sulfuric acid in the presence of potassium dichromate, chromyl chloride is formed.



This compound boils at 116° C., and can be distilled from the reaction mixture. If the vapor is caused to react with water, chromic acid is formed.



Feigl<sup>98</sup> has based an indirect method for the detection of chloride on the color reaction of diphenylcarbazide with the chromate formed in the above reaction. In this way 1.5% of chlorine can be detected at a concentration limit of 1:33,000.

Small quantities of bromides and iodides do not interfere, although larger quantities of bromide should be removed by treating the free bromine formed in the test with phenol. Nitrates interfere by forming nitrosyl chloride. Fluorides form a compound resembling chromyl chloride, and should be removed before applying the chloride test.

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95. F. Feigl, *Spot Tests*, p. 192, Nordemann (1939).
96. S. Morgulis and M. G. Hemphill, *Biochem. Z.* **249**, 409-11 (1932).
97. S. Morgulis and M. G. Hemphill, *J. Biol. Chem.* **96**, 573-83 (1932).
98. F. Feigl, *Spot Tests*, p. 159, Nordemann (1939).
99. B. B. Westfall, T. Findley and A. N. Richards, *J. Biol. Chem.* **107**, 661 (1934).
100. M. L. Isaacs, *J. Biol. Chem.* **53**, 17 (1922).
101. B. S. Evans, *Analyst.* **46**, 285 (1921); *C.A.* **15**, 3047 (1921).
102. C. F. Miller, *Chemist-Analyst.* **25**, 10-11 (1936); *C.A.* **30**, 983 (1936).
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## DIARYL CARBAZIDES

A number of carbazides have been used like diphenylcarbazide for the detection of chromates and chromic acid.<sup>1,2</sup> The test is carried out as follows:

**Procedure.** On a spot plate mix 2 drops of 0.5 N sulfuric acid solution of the chromate with 1 drop of a 0.2 per cent solution of the carbazide in acetone. With chromates the yellow color changes to a red or violet. The sensitivity of this test with the various carbazides is given in Table 83.

TABLE 83.—DETECTION OF CHROMIC ACID

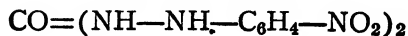
Carbazide	Sensitivity in $\gamma$
Diphenylcarbazide .....	0.02
Di-( $\alpha$ -naphthyl)carbazide .....	0.15
Di-( $\beta$ -naphthyl)carbazide .....	0.04
Di-( <i>o</i> -nitrophenyl)carbazide .....	2.0
Di-( <i>m</i> -nitrophenyl)carbazide .....	0.03
Di-( <i>p</i> -nitrophenyl)carbazide .....	0.15

For the preparation of these compounds, see section on diarylcarbazones, page 454.

1. P. Krumholz and F. Honel, *Mikrochim. Acta.* **2**, 177-83 (1937); *C.A.* **32**, 877 (1938).
2. K. Heller and P. Krumholz, *Mikrochemie.* **7**, 217 (1929).

**DINITRODIPHENYLCARBAZIDE**Synonym: *p,p'*-Dinitrodiphenylcarbazine

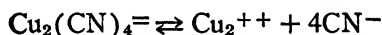
Mol. Wt. 332.23

**Use:** Detection of cadmium.

**Preparation:** Prepare a suspension of 6 g. of *p*-nitrophenyl hydrazine in 100 ml. of ether, and to this add drop by drop 12 ml. of a 20 per cent solution of phosgene in toluene. Allow the mixture to stand 6 hours, filter with suction, and wash the precipitate with ether. Finally, boil the precipitate with 0.5 N hydrochloric acid, wash with water, and dry.<sup>1</sup>

**Detection of cadmium.** Several metal hydroxides, including cadmium hydroxide, give adsorption colors with dinitrodiphenylcarbazine. Cadmium hydroxide, precipitated in the presence of the reagent, is brown in color, and on long standing this color changes to green-blue.<sup>2-4</sup>

Formaldehyde accelerates this color change, although the reason for this effect is not known. This fact proves to be a fortunate circumstance, since the use of formaldehyde makes possible the detection of cadmium in the presence of copper. This reaction is based on the difference in the stabilities of the complex cyanides of copper and cadmium in the presence of formaldehyde. Aqueous solutions of alkali cyanides react with formaldehyde to form the nitrile of glycolic acid, thereby removing the cyanide ion from solution. The complex cyanides of copper and cadmium are slightly ionized as follows:



and the concentration of the cyanide ion in solutions of the cadmium complex is sufficient to react with formaldehyde. This destroys the equilibrium, thus causing an increase in the concentration of the cadmium ions, which eventually becomes great enough to exceed the solubility product of cadmium hydroxide. The cadmium hydroxide formed in this way is especially well suited for the formation of the adsorption color with dinitrodiphenylcarbazine. Unlike the cadmium complex, however, the cuprous complex decomposes into cuprous cyanide only on heating. Thus it is seen that with the use of potassium cyanide and formaldehyde, cadmium hydroxide may be formed under conditions such that the formation of copper hydroxide is retarded.

**Procedure.** Place a drop of the solution to be tested on a spot plate and add a drop of 10 per cent sodium hydroxide, a drop of 10 per cent potassium cyanide solution, and a drop of 0.1 per cent alcoholic solution of dinitrodiphenylcarbazine and 2 drops of 40 per cent formaldehyde. Mix well. If cadmium is present, a blue-green precipitate or coloration appears. Compare with a blank if the quantity of cadmium is small. An alkaline solution of the reagent is red,



but this is colored violet with formaldehyde. By this method, 0.8γ of cadmium can be detected at a concentration of 1:62,000.

If copper is present, a sufficient excess of potassium cyanide must be used.

**Procedure.** Place a drop of solution to be tested, containing not more than 4 g. of copper in 100 ml. on a spot plate and add 1 drop of 10 per cent sodium hydroxide and 3 drops of 10 per cent potassium cyanide. Stir well until solution is complete, and add 2 drops of a 0.1 per cent alcoholic solution of the reagent and 3 drops of formaldehyde. Carry out a similar test using a 15 per cent solution of copper sulfate. In this manner 4γ of cadmium can be detected in the presence of 400 times as much copper. The concentration limit is 1:12,500.

Cadmium is best detected in the presence of ions forming insoluble hydroxides by adding ammonium hydroxide, centrifuging, and testing the supernatant liquid containing copper and cadmium. Large quantities of ammonium salts reduce the sensitivity of the reaction somewhat, but by comparing with a blank 4γ of cadmium can be detected in the presence of 250 times as much copper, and 2γ of cadmium can be detected in the presence of 120 times as much copper.

1. P. Krumholz and F. Hönel, *Mikrochim. Acta*, 2, 177 (1937).
2. I. K. Heller and P. Krumholz, *Mikrochemie*, 7, 213-22 (1929); *C.A.*, 24, 1818 (1930).
3. F. Feigl, *Qualitative Analysis by Spot Tests*, 2nd English Edition, pp. 49-50, Norde-mann, New York (1939).
4. K. Heller and F. Machek, *Mikrochemie*, 19, 147-61 (1936).

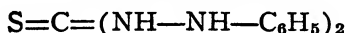
## DIPHENYLTHIOCARBAZIDE

Synonym: Diphenylthiocarbohydrazide-1,5

$C_{18}H_{14}N_4S$

Mol. Wt. 258-33

Beil. Ref. XV, 299(72).



**Use:** Detection of bismuth, cadmium, cobalt, copper, lead, magnesium, mercury, nickel and silver.

Diphenylthiocarbazine is obtained as prisms from warm alcohol. It melts at 150° C. to form a dark green liquid. It is difficultly soluble in alcohol, benzene, acetone, ether, chloroform and acetic acid.

**Preparation:** Mix 1 part of carbon disulfide with 2 parts of phenylhydrazine and shake. Wash the white precipitate 2 or 3 times with water by decantation.<sup>1,2</sup>

**Detection of magnesium, calcium and barium.** Magnesium is detected by means of a pink coloration which is obtained when an alcoholic solution of the reagent and ammonium hydroxide are added to a solution containing magnesium salts.<sup>2,3,9</sup>

**Procedure.** Add two drops of an alcoholic solution of diphenylthiocarbazine to 10 ml. of the solution to be tested, and add a large excess of ammonium hydroxide. A pink coloration appears if magnesium is present, and

the depth of the color depends on the concentration of magnesium. This reaction is sensitive to 1 part of magnesium in 300,000 parts of solution.

Calcium and barium also give reactions with diphenylthiocarbazide, but the reactions appear to be of doubtful analytical value. In the presence of sodium hydroxide calcium yields a yellow precipitate, and in an acetic acid solution a light violet color. Barium reacts similarly.

**Reactions of the heavy metals.** An alcoholic solution of diphenylthiocarbazide gives colored precipitates when added to solutions of salts of a number of the heavy metals.<sup>2,4-6,11</sup> Parri<sup>2</sup> studied the reactions obtained when a few drops of a 5 per cent alcoholic solution of the reagent are added to dilute solutions of various metallic salts. These results are reported in Table 84.

TABLE 84.—REACTIONS WITH DIPHENYLTHIOCARBAZIDE

Metal	Medium					
	Slightly Acid	Neutral	Slightly Alkaline			
Zinc	Violet ppt.	Brown ppt. Yell.-green ppt. Yellow ppt.	Red ppt.			
Chromium			Orange color			
Nickel			Brown ppt.			
Cobalt			Red ppt.			
Magnesium	Green ppt. White ppt. Light yellow ppt.	Orange ppt. Brown color Yellow ppt. Light green ppt. Red-brown ppt.	Red ppt.			
Copper			Dark blue ppt.			
Cadmium			Red ppt.			
Arsenic						
Lead	Yellow color		Violet color			
Molybdenum			Orange color			
Uranium			Orange color			
Aluminum			(KOH)—dark blue			
Silver			(NH <sub>4</sub> OH)—dark red			

A green color is obtained by heating to boiling a solution of an osmium salt and diphenylthiocarbazide.<sup>10</sup>

Diphenylthiocarbazide has also been studied as a reagent for thorium, but Wenger and Duckert<sup>8</sup> report that the reaction is not sensitive and is similar to those with uranium and the rare earths.

1. G. Heller, *Ann.* **263**, 278 (1891).
2. W. Parri, *Giorn. farm. chim.* **73**, 207-14 (1924); *C.A.* **19**, 223 (1925).
3. P. Agostini, *Ann. chim. applicata.* **20**, 235 (1930); *C.A.* **24**, 5254 (1930).
4. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713 (1929).
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6. J. V. Dubsky and J. Trtilek, *Chem. Obsor.* **9**, 142 (1934); *C.A.* **28**, 7195 (1934).
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8. P. Wenger and R. Duckert, *Helv. Chim. Acta.* **14**, 1110 (1942); *C.A.* **37**, 575 (1943).
9. K. Heller, *Mikrochem.* **9**, 451 (1931).
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**CRYOGENINE**

Synonym: 3-Semicarbazidobenzamide, *m*-benzamidosemicarbazide

$C_8H_{10}O_2N_4$

Mol. Wt. 194.19

Beil. Ref. XV, 629.



**Use:** Detection of chromate, copper, dichromate, iron, mercury, and permanganate.

Cryogenine is a white, odorless, somewhat bitter crystalline powder. It melts at about 172° C. It dissolves in 100 parts water, and is soluble in alcohol, chloroform, ether and acetone.

**Determination of copper.** Cryogenine reacts with a copper salt in a neutral aqueous solution to give a wine-red color. Concentrated copper solutions yield a precipitate. This reaction is sensitive and rather selective. Aluminum, cesium, calcium, barium, bismuth, lead, lithium, magnesium, potassium, sodium, tin, and titanium do not give either a color or precipitate with the reagent. Iron and manganese give a yellow color. The sulfates of lead, mercury and strontium give light yellow precipitates, and lead carbonate gives a colorless precipitate. Chromium, cobalt and nickel sulfates color the solution, and zinc sulfate causes a reddish-yellow color after 5-6 hours. Silver nitrate is reduced to metallic silver.

Lead acetate deepens the color caused by the reaction of cryogenine with copper. Ferrous, magnesium and sodium sulfates also intensify the copper color.

The reagent solution must be freshly prepared, since a yellow to brown color develops after a few days. Acids and bases accelerate this decomposition and cause a turbidity. For this reason the copper reaction should be carried out in a nearly neutral solution. The maximum color is developed in 30-50 minutes at a temperature of 40° C. Quantities of copper ranging from 0.0005 to 0.02 mg. can be determined with an accuracy of 1.5 per cent. High results are obtained with smaller quantities of copper, and the color is yellowish with greater quantities.<sup>1-8</sup>

**Reagent.** Dissolve 0.07 g. of cryogenine in 100 ml. of distilled water by shaking at room temperature. Store in a dark bottle, and prepare fresh every 2 days.

**Procedure.** For the analysis, use a sample or an aliquot containing 0.0005-0.03 mg. of copper. If the solution is not already acid, add 1:2 nitric acid until the mixture is distinctly acid. Evaporate to dryness in a small glass dish on a water bath, and then heat for 15 minutes to remove all excess acid.

In 3 similar dishes, place 1, 3 and 5 ml. of a standard solution containing 0.005 mg. of copper per ml. Add to each 2 ml. of 1:2 nitric acid, and dilute to the same volume as the sample. Evaporate to dryness on a water bath, and heat to remove all excess acid.

Now add to the unknown and to each sample 1 ml. of distilled water, 1 ml. of the reagent, and 1 ml. of a lead acetate solution containing 0.1831 g. per

liter. Mix thoroughly by rotating the dishes. Cover and allow to stand 40 minutes at 40° C. Compare the sample solution with that of the standard which it most nearly resembles in color. Compare in a colorimeter.

**Detection of mercury.** Cryogenine reacts with solutions of mercuric salts to form a peach-blossom color, and then a violet precipitate. When the mixture is shaken with benzene or ether, a violet ring forms at the junction of the two liquids.<sup>1</sup>

**Detection of iron.** When a cryogenine solution is added to a dilute solution of ferric chloride, and the mixture is then treated with 2-3 drops of hydrogen peroxide, a brownish-red color appears. This sensitive reaction is also obtained with ferrous salts after the addition of hydrogen peroxide.<sup>1</sup>

**Detection of permanganate.** Cryogenine reacts with potassium permanganate to give a brown color.<sup>4</sup>

**Detection of chromate.** In a concentrated solution of hydrochloric acid, chromates and dichromates produce a wine-red color when added to powdered cryogenine. An excess of chromate must be avoided.<sup>1</sup>

1. L. Bornet, *J. pharm. chim.* 30, 356-8 (1924) ; *C.A.* 19, 1388 (1925).
2. U. Sarata, *Japan J. Med. Sci. II Biochem.* 2, 247-60 (1933).
3. U. Sarata, *Japan J. Med. Sci. II Biochem.* 2, 260-75 (1933).
4. G. Pegurier, *Ann. chim. anal. appl.* 9, 456-57.

## CHAPTER XVII

### CARBAZONES

Krumholz and Honel<sup>1</sup> have prepared and investigated the analytical applications of a number of symmetrical diaryl carbazides and carbazones. These include the  $\alpha$ - and  $\beta$ -dinaphthyl- and the three isomeric di-(nitrophenyl) carbazides and carbazones. The carbazones react in a manner similar to diphenylcarbazone, and may be used for the detection of mercury, copper, iron, cadmium and molybdenum. The carbazides may be used like diphenylcarbazide for the detection of chromates

The diaryl carbazides are prepared by the action of phosgene on ether solutions of the corresponding aryl hydrazines. The carbazones are formed by the oxidation of the carbazide. The following general method may be used for the preparation of these compounds:

**Preparation:** Dissolve or suspend 0.04 moles of the hydrazine in about 50 ml. of dry ether, and add slowly with shaking a solution of 0.01 mole of phosgene in toluene. Allow the mixture to stand for a few hours after the action is completed, and then filter and remove the excess hydrazine. Boil several times with about 250 ml. of 0.1 N hydrochloric acid. Finally wash with water and dry. The carbazides thus prepared consist of yellow to brown solids.

To convert the carbazides to carbazones, suspend about 1 g. of the carbazide in 25 ml. of boiling alcohol, and mix with a concentrated solution of 1 g. of potassium hydroxide in water. The  $\beta$ -naphthyl and the *m*- and *p*-nitrophenyl derivatives are obtained after boiling for about one minute. Allow the mixture to cool and filter the separated potassium salt of the carbazone with suction. Decompose with acid, filter, wash with water and dry. The  $\alpha$ -naphthyl derivative is boiled for a few minutes, since the conversion takes place more slowly. Cool the alcoholic solution, acidify with dilute sulfuric acid, filter, wash and dry. The *o*-nitro derivative is extremely unstable and is not heated further after the addition of potassium hydroxide, but is cooled and acidified.

The carbazones obtained in this procedure are sufficiently pure for analytical purposes. The alkaline solutions are red to violet in color. The carbazides are used in the form of 0.2 per cent solutions in acetone, while the carbazones are used as 0.2 per cent solutions in methyl alcohol to which a few drops of dilute sulfuric acid have been added.

1. P. Krumholz and F. Honel, *Mikrochim. Acta*, 2, 177-83 (1937); *C.A.* 32, 877 (1938).
2. K. Heller and P. Krumholz, *Mikrochemie*, 7, 217 (1929).

#### DI- $\alpha$ -NAPHTHYLCARBAZONE



Mol. Wt. 340.34



**Use:** Detection of cadmium, copper, iron, mercury and molybdenum.

A gray-violet color appears when a drop of a neutral or 0.05 N nitric acid solution of a mercury salt is placed upon a dried strip of paper that has previously been impregnated with a 0.2 per cent solution of di- $\alpha$ -naphthylcarbazone in methyl alcohol which has been acidified with a few drops of sulfuric acid. In neutral solutions 0.05 $\gamma$  of mercury can be detected, while in the acid solution, 0.75 $\gamma$  of mercury gives a color reaction.

When a drop of a neutral solution of a copper salt is added to a test paper prepared as described above, a gray-violet color is also obtained. This test is sensitive to 0.02 $\gamma$  of copper. A similar reaction is given with iron, and the sensitivity is 0.2 $\gamma$ .

Di- $\alpha$ -naphthylcarbazone does not give a satisfactory test with cadmium in neutral or weakly acid solutions, but a sensitive test is obtained with the following procedure:

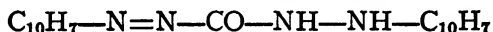
**Procedure.** On a spot plate mix 2 drops of a 0.02 per cent di- $\alpha$ -naphthylcarbazone solution with 2 drops of the cadmium solution, and add 1 drop of a saturated sodium bicarbonate solution to make alkaline. The color of the reagent changes from brown to violet in the presence of 0.4 $\gamma$  of cadmium.

The yellow solution of di- $\alpha$ -naphthylcarbazone is changed to brown upon addition to a nitric acid solution of molybdic acid. The test is carried out on a spot plate with 2 drops of a 0.1 N nitric acid solution and 1 drop of the 0.2 per cent methyl alcohol solution of the reagent. Five  $\gamma$  of molybdenum is detected in this way.

### DI- $\beta$ -NAPHTHYLCARBAZONE



Mol. Wt. 340.34



**Use:** Detection of cadmium, copper, iron, mercury and molybdenum.

Di- $\beta$ -naphthylcarbazone is used like di- $\alpha$ -naphthylcarbazone for the detection of mercury, iron, copper, cadmium and molybdenum. The reactions are carried out in a similar manner. With 0.015 $\gamma$  of mercury in a neutral solution, di- $\beta$ -naphthylcarbazone gives a violet color. The reagent also gives a violet color with 0.003 $\gamma$  of copper and 0.02 $\gamma$  of iron in neutral solutions.

Heller and Krumholz<sup>2</sup> have suggested the use of *p*-nitrophenylcarbazide as a reagent for cadmium (page 449). The carbazide used in this reaction is oxidized to the carbazone in an alkaline solution, and it is this compound which is responsible for the cadmium test. Krumholz and Honel<sup>1</sup> now report that di- $\beta$ -naphthylcarbazone is a more suitable reagent for the detection of cadmium. In the presence of copper the excess reagent is almost completely decolorized, while the cadmium compound remains stable. For the detection of cadmium in the presence of copper, proceed as follows:

**Procedure.** To 2 drops of a neutral or weakly acid solution, which should contain not more than 0.5 per cent of copper, add 1 drop of 2 N sodium hydroxide and 1 drop of 10 per cent potassium cyanide solution. When all the copper

hydroxide has dissolved, add 2 drops of 0.02 per cent methyl alcohol solution of di- $\beta$ -naphthylcarbazone and 2 drops of 40 per cent formaldehyde. Mix well. In the absence of cadmium, the color of the reagent disappears within a few minutes, but if cadmium is present a more or less intense violet precipitate is formed, which after a few minutes is particularly noticeable. By means of this method, 0.1 $\gamma$  of cadmium is detected in the presence of 5000 times as much copper. Ammonia and ammonium salts in higher concentrations interfere with this reaction.

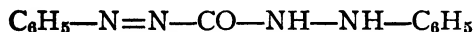
Molybdic acid is detected by a procedure similar to that described with di- $\alpha$ -naphthylcarbazone. As little as 0.3 $\gamma$  of molybdic acid changes the yellow color of the reagent to violet.

### DIPHENYLCARBAZONE

$C_{18}H_{12}ON_4$

Mol. Wt. 240.26

Beil. Ref. XVI, 24(222).



**Use:** Detection of cadmium, chromium, copper, iron, mercury and molybdenum.

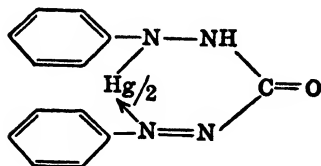
Determination of lead, mercury and zinc.

Diphenylcarbazone consists of orange-red needles which melt at about 157° C. with decomposition. It is insoluble in water but dissolves in alcohol, chloroform and benzene.

**Preparation:** Dissolve 24 g. of diphenylcarbazide (page 430) by boiling for 15 minutes with 200 ml. of 95 per cent alcohol in a liter flask. To the hot solution, add all at once and with stirring, 20 g. of powdered potassium hydroxide. Then add 20 ml. of 3 per cent hydrogen peroxide. Allow the mixture to stand for 5 minutes and add 250 ml. of 2 N sulfuric acid while stirring. Pour the paste into a 3-liter vessel and add 1500 ml. of water to dissolve the potassium sulfate. Cool completely, filter, and wash thoroughly with water and then dry.<sup>1</sup>

**Reactions of metals.** In 1888 Skinner and Ruhemann<sup>2</sup> observed the diphenylcarbazone formed salts with a number of metals. These reactions were later recommended by Cazeneuve<sup>3-5</sup> for the detection of several of the heavy metals. The zinc, lead, ferrous and cobalt salts of diphenylcarbazone are cherry-red in color; the copper compound is violet; and the mercuric compound is blue. All of these are soluble in alcohol, benzene and carbon disulfide, but are insoluble in chloroform. Gold yields a blue-violet compound and platinum chloride a red compound. The reagent reduces gold chloride.<sup>3-5</sup> Fischer<sup>6,7</sup> has also studied the metal complexes of diphenylcarbazone.

Two series of salts are possible for diphenylcarbazone: one is derived from the keto form and the other is derived from the enol modification. The more intensely colored chelate salts, however, are derived from the keto form and their composition may be represented by the formula for mercuric compound



Since diphenylcarbazone is formed by the oxidation of diphenylcarbazide, even in air, Cazeneuve<sup>3-5</sup> and others have suggested that perhaps the colored complexes formed with the latter are in reality due to the presence of diphenylcarbazone as an oxidation product. Cazeneuve<sup>5</sup> states that the copper and mercury compounds of diphenylcarbazone are formed when diphenylcarbazide is added to solutions of the metallic salts. Menier<sup>8,9</sup> first recommended the use of diphenylcarbazide for the determination of mercury, and Stock and co-workers<sup>10,11</sup> suggested replacing diphenylcarbazide with diphenylcarbazone, which according to them is the compound which yields the color reaction with mercury.

Feigl and Lederer<sup>12,13</sup> report that when oxidized diphenylcarbazide yields diphenylcarbazone and diphenylcarbadiazone ( $(C_6H_5-N=N)_2CO$ ). They report that the products formed by the action of metal salts and diphenylcarbazide are in reality carbazides and not carbazones as reported by Cazeneuve.<sup>14</sup> It appears likely, however, that under the conditions of many tests involving diphenylcarbazide that diphenylcarbazone is present as an oxidation product.

Krumholz and Honel<sup>15</sup> have studied the use of diphenylcarbazone for the detection of mercury, copper, iron, cadmium and molybdenum. A violet color appears when a drop of a neutral solution of a mercury salt is placed upon a strip of filter paper that has been impregnated with a 0.2 per cent solution of diphenylcarbazone in methyl alcohol which contains a few drops of sulfuric acid. This test is sensitive to 0.05 $\gamma$  of mercury. Iron and copper can be detected by the same procedure, although the color obtained with these metals is red. In this way 0.005 $\gamma$  of copper and 0.05 $\gamma$  of iron can be detected. Cadmium does not react well in a neutral or acid solution, but if the reaction is carried out in an alkaline medium and on a spot plate, 0.5 $\gamma$  of cadmium can be detected by the red-violet color which forms. Sodium bicarbonate is used to neutralize the mixture. If 2 drops of a 0.1 N nitric acid solution of a molybdate is mixed with 1 drop of a 0.2 per cent methyl alcohol solution of diphenylcarbazone, the yellow reagent changes to a rose color with 2.5 $\gamma$  of molybdenum.

Dubsky<sup>16</sup> has also studied the use of this reagent for the detection of mercury. Thompson<sup>17</sup> has used diphenylcarbazone for the detection of mercury in a coloroscopic technique of analysis,

Miller and Lowe<sup>18</sup> have used diphenylcarbazone as a confirmatory test for mercury in a systematic scheme of analysis. The metals included in this scheme are gold, mercury, palladium, platinum and iridium. Mercury is detected in the following manner:

**Procedure.** Evaporate the solution of the above metals in aqua regia to 0.1 ml. on a steam-bath, and dissolve the residue in 3 ml. of water. Add 1 drop of N hydrochloric acid, and extract with 1.5 ml. of ethyl acetate. Repeat the



extraction, and evaporate the ester extracts to dryness on a steam-bath. Take up in 3 N hydrochloric acid, and to a part of this solution add water and treat with sulfur dioxide. Digest in hot water and filter. Evaporate the filtrate to dryness and dissolve in 0.5 ml. of water. Add an excess of sodium acetate, and adjust the pH to 7-8 by adding 1 drop of a 0.02 per cent alcoholic solution of phenol red and then dilute sodium hydroxide until the mixture assumes a pink tinge. Then test with a saturated alcoholic solution of diphenylcarbazone. A purple solution or precipitate is obtained if mercury is present. Five  $\gamma$  of mercury is detectable by this procedure.

Palladium reacts like mercury, while gold yields a black precipitate. Platinum, rhodium and iridium in quantities up to 500 $\gamma$  in 0.5 ml. of solution give no reaction.

Grosset<sup>19</sup> has used diphenylcarbazone for the detection of chromium in a systematic scheme of analysis. The reaction is similar to that described in the section on diphenylcarbazide (page 431).

**Determination of mercury.** The blue color which is formed with mercury and diphenylcarbazone may be used for the determination of 0.0005-0.01 mg. of mercury. This reaction was first used by Meniere<sup>8</sup> who used diphenylcarbazide, and later by Stock and co-workers,<sup>10,11</sup> and by Bodnar and Szep.<sup>20</sup> The potassium derivative of diphenylcarbazone forms scarlet to blue salts with zinc, lead, copper, mercury, chromium, iron, nickel and cobalt. For this reason it is necessary that mercury be separated from other heavy metals before applying the colorimetric test. Since the determination of small quantities of mercury is often applied to the analysis of tissues or other organic matter, or for determining the mercury content of air, procedures are given for preparing these materials for analysis:

**Procedure.** Grind 100-200 g. of tissue or other organic material with water to form a semi-liquid paste, and add to the finely divided material a quantity of potassium chlorate equal to 10 per cent of the weight of sample taken, and finally add a quantity of hydrochloric acid equal to 20 per cent of the weight of sample. Heat until the organic matter is destroyed, and arrange to pass the gas evolved during this process into water to absorb mercuric chloride. Filter and wash the residue on the filter with the solution used for the absorption of mercuric chloride. Reduce the potassium chlorate and arsenic compounds in the filtrate with sulfurous acid, and boil for a few minutes to remove any excess of sulfur dioxide. Then pass a slow current of hydrogen sulfide through the solution for 18 hours and collect the precipitated sulfides by filtration.

The mercury is separated from the other heavy metals present by the following procedure: Dissolve the mixed sulfides in aqua regia and evaporate to dryness in vacuum. Dissolve the residue with warm water and filter into a test tube. Dilute to 20 ml. and add 1 ml. of concentrated hydrochloric acid, and saturate the solution with pure ammonium oxalate. Then introduce into the solution a piece of pure copper wire of such length that it is not completely immersed in the solution. Electrolytic copper is best for this determination. Heat the upper part of the tube containing the solution and the wire and draw out

the tube until the two sections are connected by a rather narrow neck. Evacuate with a water pump and seal the tube by heating the neck. The purpose of this operation is to exclude air and prevent oxidation of the copper. Warm the sealed tube for 24-36 hours at 50-60° C. and then break the tube and remove the wire, upon which the mercury has been deposited. Wash by immersing in several successive portions of distilled water. Avoid stirring. Finally, dry over phosphorous pentoxide at room temperature for 3 hours.

Distill the mercury from the wire, which is placed in a hard glass tube having a capillary constriction in the middle and drawn out to a fine capillary at the end. Heat the closed end, which contains the wire, for 5 minutes while cooling the open end of the tube in running water which serves to condense the mercury. Avoid fusing the wire to the glass. Cut off the tube at the narrow part.

Connect one end of the tube to a suction pump and the other end to a source of chlorine gas which is dried by passing through sulfuric acid. Pass chlorine through the tube until practically all air has been replaced by chlorine and then fuse the tips of the capillary. Heat the sealed tube throughout its entire length at 250° C. for 15 minutes, during which time the mercury is converted to mercuric chloride. Now move the tube in the heating element so that one of the capillaries projects from the holder, and while cooling this part in water, heat the rest of the tube for 3 hours at 250-300° C. The mercuric chloride is condensed in the exposed part. Now allow the tube to cool and open the end which does not contain the salt, and connect with a suction pump and evacuate the excess chlorine. Disconnect from the pump and allow to fill with air and repeat the evacuation several times until all free chlorine has been removed. Heat the tip of the closed capillary so that the mercuric chloride is sublimed away from the extreme tip and remove this.

Draw 2 ml. of water into the tube to dissolve the mercuric chloride, and then add 2 drops of a cold saturated solution of urea and 1 drop of the alcoholic potassium diphenylcarbazone reagent. The color increases for 10-15 minutes and then remains constant for several hours. When the color reaches a maximum, compare with that of standards similarly prepared. Yellow light is most satisfactory for the comparison.

The reagent is prepared by boiling 1 part by weight of diphenylcarbazide with 1 part of potassium hydroxide in 5 parts by weight of 95 per cent alcohol for 10 minutes.

The standard mercury solution is prepared as follows: Dissolve 0.1354 g. of mercuric chloride in distilled water and dilute to 1 liter. Dilute 100 ml. of this solution to 1 liter, and a second portion of 10 ml. to 1 liter. These two solutions contain 0.01 and 0.001 g. of mercury per ml. respectively. A series of 2 ml. standards containing 0.01, 0.008, 0.006, 0.004, 0.002, 0.001 and 0.0005 mg. of mercury is prepared from suitable volumes of the standard. Treat with 2 drops of a cold saturated solution of urea and 1 drop of the reagent.

Mercury in air may be determined by absorbing the mercury vapor in air by passing through chlorine water. The mercury may be precipitated on a copper wire and determined as described above. The removal of chlorine from

a solution of mercuric chloride in chlorine water presents some difficulty. The most satisfactory method seems to be the evaporation of the solution in a desiccator containing phosphorous pentoxide and soda lime. If the solution is evaporated completely to dryness, some mercuric chloride is lost, and this error may be eliminated by evaporating to a volume of 0.05-0.5 ml.<sup>21</sup> Some investigators have recommended the removal of the excess chlorine by passing air through the solution, but this results in the volatilization of some mercuric chloride, and a consequent error in the final determination.

Heavy metals, acids, free chlorine and salts of the light metals must be removed. Even small quantities of electrolytes interfere by causing a flocculation of the colloidal material.<sup>22</sup>

Alekseev<sup>23</sup> has studied the methods for the colorimetric determination of mercury with diphenylcarbazide and diphenylcarbazone, and reports that the latter is more satisfactory because of its greater purity and resulting uniformity of color reaction. The determination of mercury with diphenylcarbazone in the presence of other elements capable of giving a similar color reaction may be carried out in the presence of sodium pyrophosphate, which forms complex compounds with interfering elements. Alekseev<sup>23</sup> reports that the optimum pH for mercury determination with diphenylcarbazone is 7.0. Vasserman and Spurnovich<sup>24</sup> have attempted to apply the principle of colorimetric comparison to solutions of the heavy metal complexes of diphenylcarbazone in organic solvents, but they report that these methods are unreliable. They suggest, however, that lead, mercury and zinc can be determined gravimetrically as diphenylcarbazone complexes.

Diphenylcarbazone has also been used as an indicator in mercurimetry.<sup>25-28</sup>

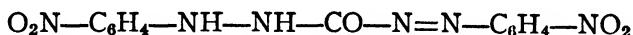
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## THE NITROPHENYLCARBAZONES

$C_{13}H_{10}O_5N_6$

Mol. Wt. 330.21



**Use:** Detection of cadmium, copper, iron, mercury and molybdenum.

The three isomeric nitrophenylcarbazones may be used for the detection of mercury, iron, copper, cadmium and molybdenum. To detect mercury, add a drop of a neutral or 0.05 N nitric acid solution of the mercury salt to filter paper that has been impregnated with a 0.2 per cent solution of the carbazone in methyl alcohol and allowed to dry. The results are given in Table 85.

TABLE 85.—DETECTION OF MERCURY

Carbazone	Sensitivity of Test in $\gamma$		Color of Reaction Product
	Neutral	Acid	
Di-( <i>o</i> -nitrophenyl) carbazone .....	0.08	1.0	Gray-blue
Di-( <i>m</i> -nitrophenyl) carbazone .....	0.05	0.4	Red-brown
Di-( <i>p</i> -nitrophenyl) carbazone .....	0.025	0.4	Blue

Copper and iron are detected by a procedure similar to that used for mercury. The results are given in Table 86.

TABLE 86.—DETECTION OF IRON AND COPPER

Carbazone	Sensitivity in $\gamma$				Color of Reaction Product.
	Copper		Iron		
	Neutral	Acid	Neutral	Acid	
Di-( <i>o</i> -nitrophenyl) carbazone ....	0.002	1.0	0.1	50	Violet
Di-( <i>m</i> -nitrophenyl) carbazone ...	0.002	0.05	0.025	0.2	Red
Di-( <i>p</i> -nitrophenyl) carbazone ....	0.0015	1.0	0.025	2.5	Blue-violet

These carbazones do not react satisfactorily with cadmium in a neutral or acid solution, but in a solution that has been made alkaline with sodium hydroxide a sensitive test may be obtained with the *m*- and the *p*-nitrophenyl derivatives. The test is carried out as follows:

**Procedure.** On a spot plate mix 2 drops of a 0.02 per cent solution of the nitrophenylcarbazones in methyl alcohol with 2 drops of a cadmium solution and a few drops of a 2 N sodium hydroxide solution. With *m*-nitrophenylcarbazone 0.7 $\gamma$  of cadmium can be detected by the change in color of the orange reagent to violet. The red-violet *p*-nitro derivative is changed to blue-violet, by 0.5 $\gamma$  of cadmium.

Molybdic acid can be detected by a drop reaction with *m*-nitrophenylcarbazone and *p*-nitrophenylcarbazone. These reactions are sensitive to 0.5 $\gamma$  of molybdenum. The test is carried out by mixing 2 drops of a 0.1 N nitric acid solution to be tested with 1 drop of a 0.2 per cent methyl alcohol solution of the carbazone.

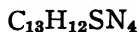
## CHAPTER XVIII

### THIOCARBAZONES

Only two members of this group have been used as analytical reagents: these are diphenylthiocarbazone (dithizone), and di- $\beta$ -naphthylthiocarbazone. These compounds, especially the former, have proved extremely useful in inorganic analysis.

#### DIPHENYLTHIOCARBAZONE

Synonym: Dithizone



Mol. Wt. 256.32

Beil. Ref. XVI, 26.

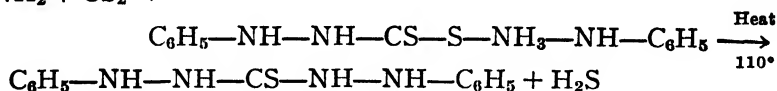


**Use:** Detection of bromine, cadmium, cobalt, copper, lead, mercury, silver and zinc.

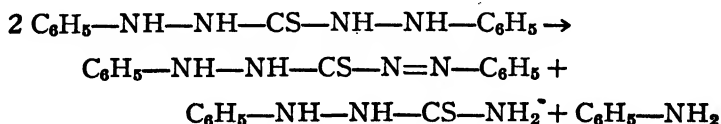
Determination of bismuth, cadmium, cobalt, copper, lead, mercury, silver, and zinc.

Dithizone is obtained as purplish black rods or needles from chloroform. It is readily soluble in chloroform and to a lesser extent in carbon tetrachloride. It is insoluble in water and dilute mineral acids, but is readily soluble in dilute ammonium hydroxide.

**Preparation of dithizone:** Diphenylthiocarbazone (dithizone) was first prepared and studied by Emil Fischer <sup>1,2</sup> during an investigation of the structure and reactions of phenylhydrazine. This preparation consists of treating phenylhydrazine with carbon disulfide to form phenylhydrazine phenylthiocarbazinate, which upon heating decomposes to diphenylthiocarbazide:



Upon heating the carbazide with an alcoholic potassium hydroxide solution, a mutual oxidation-reduction reaction occurs in which diphenylthiocarbazone and phenylthiosemicarbazide are formed. This is illustrated by the following equation:



Dithizone is prepared by the following procedure:

**Procedure.** Dissolve 2 moles of phenylhydrazine in 4 volumes of anhydrous ether, and then add slowly 1 mole of carbon disulfide, also dissolved in

ether. These reagents react rather violently to form a white precipitate of phenylhydrazine phenylthiocarbazonate. Filter this compound and wash with ether. Press out as much ether as possible and dry in air, and then heat in a thin layer on an oil-bath at 100-110° C. Continue heating until hydrogen sulfide is no longer evolved and the odor of ammonia appears. Wash the crude product with alcohol and then boil the residue of diphenylthiocarbazide for about 15 minutes with 2 N alcoholic potassium hydroxide. Filter the dark-red solution, and to the filtrate add dilute sulfuric acid until the precipitation of diphenylthiocarbazone is complete. Dry the blue-black product over sulfuric acid or magnesium perchlorate in a desiccator.<sup>1,2,4,5</sup>

The following improved method is taken directly from the published work of Billman and Cleland.<sup>184</sup>

**Preparation: Phenylhydrazine Salt of  $\beta$ -Phenyldithiocarbazic Acid:** In a 1-liter three-necked flask, fitted with a motor stirrer, a condenser and a dropping funnel, is placed 128 cc. (sp. gr. 1.097) of pure redistilled phenylhydrazine, dissolved in 600 cc. of ordinary ether. The mixture is stirred vigorously during the addition of 52 cc. of carbon disulfide (sp. gr. 1.26), which is added at the rate of two drops per second, taking about one-half hour in all. The flask should be cooled with ice water whenever the mixture tends to boil. The stirring is continued for another half hour after addition of all the carbon disulfide. The precipitate is filtered by suction, and washed with 50 cc. of ether. It is then spread out on filter paper for fifteen to twenty minutes to allow evaporation of the ether. The yield is 183 g. (97%, based on phenylhydrazine).

**Diphenylthiocarbazide:** The above salt is transferred to a 1-liter beaker and heated under a hood in a water-bath that is kept between 96-98°. *Caution*—do not heat above 98°. A heavy glass rod, bent or flattened at the end, acts as an efficient stirrer. The powder is stirred continuously by hand. After about ten to fifteen minutes the compound melts, becomes yellow and foamy, and liberates hydrogen sulfide. After about twenty to thirty minutes ammonia is given off. When a distinct odor of ammonia is *first detected*, the beaker is removed from the hot bath and placed in a pan of cold water for a minute and then cooled with cracked ice immediately. If the compound is heated as high as 100°, and allowed to stand without immediate cooling after removal from the water-bath, the compound decomposes violently. The mass may be olive green or brown when the heating is stopped, but it turns light brown on cooling. About 150 cc. of absolute alcohol is added, the mixture is warmed slightly to loosen the mass, and then stirred until the taffy-like material has changed to a granular white precipitate. The mixture is allowed to stand at room temperature for one hour. The precipitate is collected on a Büchner funnel and washed with 50 cc. of absolute alcohol. If the red alcoholic filtrate is allowed to evaporate slowly, more of the carbazide will precipitate out. The yield of crude diphenylthiocarbazide is 100-125 g. (60-75%, based on the phenylhydrazine).

**Diphenylthiocarbazone:** The crude carbazide is added to a solution of 60 g. of potassium hydroxide in 600 cc. of methanol in a 1-liter round-bottomed flask.

The flask is heated in a water-bath until refluxing takes place. The mixture is refluxed for exactly five minutes, after boiling begins. (If it is boiled for a longer time, the yield is decreased.) The red solution is cooled with ice water and filtered by gravity. The carbazone is precipitated by adding ice-cold 1 N sulfuric acid with stirring, until the solution just tests acid to congo red paper. About 900-1100 cc. is necessary. When the end-point is reached, the liquid is no longer red but colorless. The blue-black precipitate is filtered by suction and washed with 50 cc. of cold water. The crude carbazone is recrystallized by dissolving it in 500 cc. of 5% sodium hydroxide solution, filtering by suction and acidifying immediately with 1 N sulfuric acid (about 650 cc.) until just acid to congo red paper. The precipitate is filtered by suction and then washed thoroughly with water by transferring it to a 2-liter beaker, adding 1600-1800 cc. of cold water, stirring thoroughly and refiltering. This process is repeated until there is no trace of sulfate in the washings. Four or five washings are usually necessary. Air is drawn through the precipitate on the Büchner funnel for twenty to thirty minutes. It is then dried in an oven at 40°. The yield of this crude diphenylthiocarbazone is 63-85 g. (75-102% based on phenylhydrazine). The decomposition range is anywhere from 120-140°. The carbazone is purified by putting a 5-10 g. portion of it in a Soxhlet extractor, covering with ether, allowing it to stand one hour, and then extracting one and one-half hours. The product is transferred immediately to a beaker, washed again with 50 cc. of ether, filtered by suction just long enough to remove most of the liquid, and then further dried by pressing between filter paper. The recovery is 60-87%. The purer the crude dithizone, the higher the percentage recovery. The pure compound is completely soluble in chloroform and decomposes sharply at a temperature between 165-169°.

The over-all yield of pure diphenylthiocarbazone based on the phenylhydrazine is 43-54.8 g. (52-66%).

**Oxidation of dithizone.** In the presence of mild oxidizing agents, dithizone is converted to diphenylthiocarbadiazone.<sup>10</sup>



This compound is insoluble in acid and basic aqueous solutions, but dissolves readily in chloroform and carbon tetrachloride to form a yellow or brown solution. Because of the absence of acidic hydrogen atoms in the molecule, it does not react with metals to form complex salts.

In certain analytical procedures, complications may arise as a result of the oxidation of dithizone by oxidizing agents present in the unknown solution. Ferric iron oxidizes dithizone, especially in alkaline solutions containing citrate or tartrate, and also in alkaline cyanide solutions. Copper in alkaline cyanide solutions also oxidizes dithizone. Other substances capable of forming the yellow oxidation product of dithizone are the halogens, permanganate, and nitrous acid. Dithizone is decomposed by the action of strong oxidizing agents. If dithizone has been oxidized only partially to diphenylthiocarbadiazone, the reagent may be regenerated by the reducing action of sulfur dioxide or hydroxyl-



amine hydrochloride. In order to prevent interference by oxidizing agents in analytical procedures, hydroxylamine hydrochloride is often added to the solution containing the metallic salt as a preliminary to extraction with a chloroform or carbon tetrachloride solution of dithizone. Frequently a preliminary extraction of the metal is necessary to avoid interference due to oxidizing agents.

**Purification of dithizone.** The preparation of dithizone is comparatively simple but the product is seldom obtained in a pure state. The commercial product usually contains as impurities sulfur, the carbazide, and yellow to brown oxidation products. These impurities are not soluble in dilute ammonium hydroxide, while dithizone dissolves readily. To purify the reagent, therefore, it is necessary only to shake a chloroform solution with ammonium hydroxide, separate the aqueous layer, and acidify to precipitate pure dithizone.

**Procedure.** Dissolve 1 g. of commercial dithizone in 50-75 ml. of chloroform and filter from any insoluble material which may be present. Extract with four 100-ml. portions of metal-free, redistilled 1:99 ammonium hydroxide. The dithizone passes into the aqueous layer to form an orange colored solution. Filter the aqueous extracts into a large separatory funnel through a small plug of cotton inserted in the stem of the funnel. Make the filtrate slightly acid with dilute hydrochloric acid, and extract the precipitated dithizone with 2 or 3 20-ml. portions of chloroform. Combine the extracts in a separatory funnel and wash 2 or 3 times with water. Evaporate the chloroform layer in a beaker on a steam-bath at low heat until all of the chloroform is removed. Remove the last traces of moisture by heating for an hour at a temperature not exceeding 50° C. *in vacuo*. Store the dry reagent in a dark, tightly stoppered bottle.<sup>6,7,8</sup>

The test for purity of the reagent consists of extracting a strong chloroform solution with dilute metal-free ammonium hydroxide and observing the final color of the chloroform layer. If this is water-white, the reagent may be regarded as pure, but a light yellow to brown color in the chloroform layer indicates the necessity for purification.<sup>9</sup>

In most of its analytical applications, dithizone is used in a chloroform or carbon tetrachloride solution. The pure reagent may be prepared by the procedure described above, but the chloroform or carbon tetrachloride solution may be rendered slightly impure by oxidation. Both chloroform and carbon tetrachloride solutions of dithizone decompose rapidly with the formation of diphenylthiocarbazone when exposed to strong light, or when heated to relatively high temperatures. Direct sunlight bleaches dithizone solutions rapidly. According to Clifford,<sup>12</sup> sunlight causes the decomposition of chloroform into such substances as phosgene, which in turn cause the oxidation of dithizone. Due to oxidation, some difficulty is encountered in preparing and storing stock solutions of dithizone. Wichmann<sup>11</sup> has stated that a solution of pure dithizone in chloroform or carbon tetrachloride is stable for a time if protected from direct sunlight and stored in a cool place. Fischer and Leopoldi<sup>8</sup> recommend the use of a dilute solution of sulfur dioxide in water to reduce the oxidized compound

to dithizone. Clifford<sup>12</sup> claims that a solution of sulfur dioxide will not preserve a carbon tetrachloride solution of dithizone indefinitely, but that by overlaying a stock solution of dithizone in chloroform with 0.1 M solution of sulfur dioxide, the reagent remains unchanged for months if stored in the dark at ice box temperature.

**Recovery of chloroform.** The use of dithizone in many analytical procedures requires comparatively large quantities of chloroform for the preparation of the reagent, and for the extraction of metal dithizonates. Biddle<sup>13</sup> has proposed the following scheme for the recovery of chloroform that has been used in these procedures, and the product has been found suitable for further use.

**Procedure.** Remove any aqueous layer that may be present, and wash until colorless with commercial sulfuric acid, which is equal to 5-10 per cent of the volume of chloroform. Treat with calcium hydroxide, and distill in the presence of an excess of calcium hydroxide. Use an all-glass apparatus for the distillation. Finally add to the distillate 1.0-1.5 per cent by volume of alcohol as a preservative. This product is satisfactory for use in analytical procedures employing dithizone.

This method is also used for improving the quality of U.S.P. chloroform. Carbon tetrachloride is purified in the same way, but alcohol is not added as a preservative.

Biefeld and Patrick<sup>14</sup> report that chloroform that has been recovered a number of times by this method is not entirely satisfactory for further use. Solutions of dithizonates containing chloroform that has been recovered a number of times becomes cloudy on standing a few minutes after extraction. The cause of this appears to be the accumulation of a fairly high percentage of alcohol, and this results in a greater absorption of water. Consequently, Biefeld and Patrick<sup>14</sup> recommend that little or no additional alcohol be added as a preservative after the first reclamation process. They also advise refluxing any chloroform in which there is a suggestion of phosgene formation for two or three hours before the final distillation.

**Reactions of dithizone with metals.** Dithizone was first prepared by Emil Fischer,<sup>2</sup> who observed its acid character and reported the formation and the color of its zinc salt. There is no report of any attempt to use dithizone as an analytical reagent until 1925 when Hellmut Fischer<sup>137</sup> began a series of investigations of the metallic dithizonates, and their possible applications in analytical chemistry.

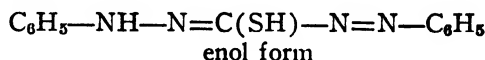
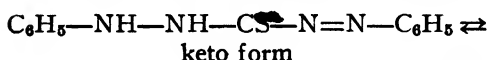
Dithizone is a violet-black solid which dissolves in most organic liquids, at least to some extent. It is only slightly soluble in hydrocarbons, but dissolves readily in chloroform and less so in carbon tetrachloride. The latter two liquids are used exclusively in the preparation of solutions of dithizone for analytical purposes.

Dilute solutions of dithizone in these liquids are green in color, but more concentrated solutions are red in transmitted light and green in reflected light. In strongly polar solvents, such as nitrobenzene, dithizone is yellow. When a

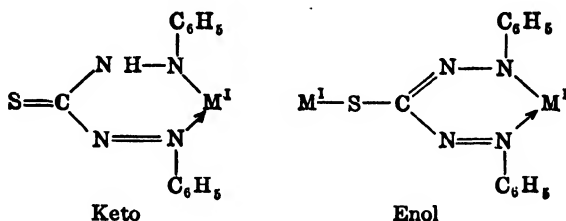
solution of dithizone in chloroform or carbon tetrachloride is shaken with an aqueous solution of a salt of a heavy metal, such as lead, cobalt, zinc, cadmium, mercury and silver, a complex salt is formed, which is usually soluble in the organic liquid, and imparts to it colors ranging from violet, through red and orange to yellow, depending on the metal present.<sup>10,15,16</sup>

Dithizone and its metallic salts, the so-called dithizonates, are essentially insoluble in neutral and acidic aqueous solutions. In alkaline solutions, however, dithizone dissolves to form a yellow solution containing the alkali metal dithizonate. The dithizonates are more soluble in chloroform and carbon tetrachloride than in aqueous solutions.

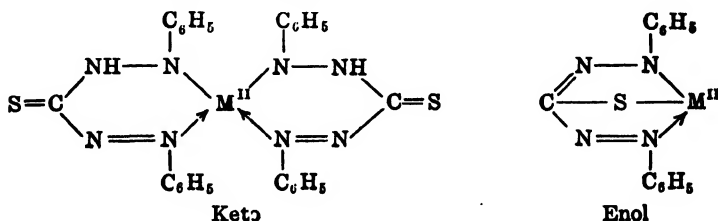
**The metal dithizonates.** Dithizone exists in two tautomeric forms.



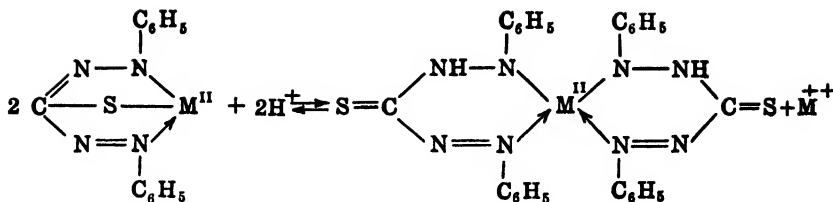
In the keto form, the hydrogen atom of the imide group of dithizone is replaced by the metal, and in the enol form the hydrogen atom of the sulfhydryl group is also replaced. Consequently, the enol form contains 2 times as much metal as the corresponding keto form. The formulas for the keto and enol forms of the monovalent metal dithizonates are:<sup>3</sup>



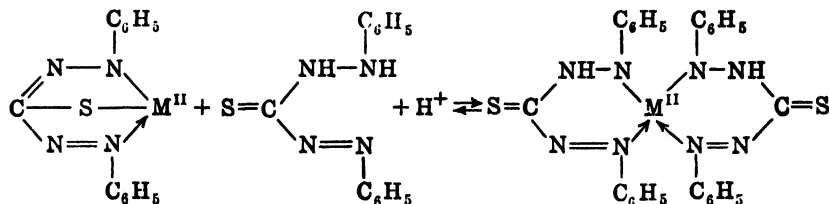
The formulas for the dithizonates of bivalent metals are:



According to Fischer, the keto forms of all metal dithizonates exist, but many of the enol forms are not known. The keto tautomer is preferentially formed in an acid or neutral solution, while the enol modification is formed either in an alkaline solution or with a deficiency of dithizone. The enol form is transformed into the keto tautomer by treating with an acid:



or by treating with an acid and dithizone.



The keto tautomer can be converted more or less readily into the enol form, if this exists, by treating with a base. The keto form of the reagent is the most important analytically.<sup>16</sup>

According to Fischer,<sup>17</sup> dithizone yields precipitates in alkaline or ammoniacal solutions with copper, silver, gold, zinc, cadmium, mercury, thallium, tin, lead, manganese, iron, nickel, cobalt, ruthenium, rhodium, palladium, osmium, iridium and platinum. These compounds are all soluble in chloroform, carbon tetrachloride and carbon disulfide.

Table 87, prepared by Clifford<sup>18</sup> and taken from the work of Fischer<sup>10</sup> and Fischer and Weyl<sup>15</sup> contains important information regarding the composition, formation, and description of various metal dithizonates.

Dz in the above formulas has been suggested by Hibbard<sup>19</sup> as a symbol for the anion of dithizone in metal dithizonates.

Liebhafsky and Winslow<sup>20</sup> have reported that lead dithizonate corresponds to the formula PbDz, but Clifford<sup>18</sup> has shown that the compound is actually PbDz<sub>2</sub>.

**Selectivity of the dithizone reaction.** Despite the fact that dithizone gives distinctive reactions with copper, silver, gold, zinc, cadmium, mercury, thallous, stannous, lead, bismuth, manganous, cobalt, nickel, palladium, and platinum salts, by controlling the conditions of the reaction, interference by the various metals can largely be eliminated, thereby making possible many tests and determinations of individual ions.

In general, the analytical applications of dithizone are based on the extraction of the metals to be detected or determined by shaking the chloroform or carbon tetrachloride solution of the reagent with an aqueous solution of the metallic salt. This operation may be carried out for the purpose of concentrating the metal, or of separating it from interfering substances, or else as a step in the actual determination. In any case, the completeness of the extraction and the selectivity of the reaction become a matter of critical importance.

TABLE 87.

Cation	Complex Form	pH for Extraction	Color in Solvent (CCl <sub>4</sub> unless otherwise stated)
Cu <sup>2+</sup>	Keto-CuDz <sub>2</sub>	0.1 N acid	Violet-red
Cu <sup>2+</sup>	Enol-CuDz	Alkaline	Greenish-brown
Cu <sup>+</sup>	Keto?	0.1 N Acid	Red-brown to violet
Cu <sup>+</sup>	Enol?	Alkaline	Green-brown (probably Cu <sup>2+</sup> compound)
Ag <sup>+</sup>	Keto-AgDz	Dil. acid	Yellow
Ag <sup>+</sup>	Enol-Ag <sub>2</sub> Dz	Alkaline	Violet (insoluble)
Au <sup>+</sup>	Keto-AuDz	Dil. acid	Dirty yellow (partially insoluble)
Au <sup>+</sup>	Enol-Au <sub>2</sub> Dz	Alkaline	Reddish insoluble
Zn <sup>2+</sup>	Keto-ZnDz <sub>2</sub>	Neutral or weakly alkaline	Reddish-purple
Hg <sup>2+</sup>	Enol-HgDz	Weakly alkaline	Violet
Hg <sup>2+</sup>	Keto-HgDz <sub>2</sub>	Dil. acid	Yellow
Hg <sup>+</sup>	?	Alkaline	Weak colors simulating Hg <sup>2+</sup> compounds, probably due to oxidation
Hg <sup>+</sup>	?	Acid	
In <sup>3+</sup>	.....	5-6	Red
Tl <sup>+</sup>	Keto-TlDz	9-12	Red
Tl <sup>3+</sup>	.....	3-4 incomplete	Gold red
Pb <sup>2+</sup>	Keto-PbDz <sub>2</sub>	8-11.5 (CHCl <sub>3</sub> )	Cherry-red
Bi <sup>3+</sup>	Keto-BiDz <sub>3</sub>	>2 (CCl <sub>4</sub> )	Orange
Bi <sup>3+</sup>	Enol	Alkaline	Orange-red
Sn <sup>2+</sup>	Keto-SnDz <sub>2</sub>	>4 (Optimum 6-9 in CCl <sub>4</sub> )	Purple-red
Mn <sup>2+</sup>	.....	11 (Unstable)	Brownish-red (soluble in CHCl <sub>3</sub> , insoluble in CCl <sub>4</sub> )
Fe <sup>2+</sup>	.....	6-7 (CCl <sub>4</sub> )	Violet-red
Co <sup>2+</sup>	Keto-CoDz <sub>2</sub>	7-9 (CCl <sub>4</sub> )	Violet
Ni <sup>2+</sup>	Keto-NiDz <sub>2</sub>	Weakly alkaline	Dirty brown
Pd <sup>2+</sup>	Enol-PdDz	Weakly acid	Violet or brown
			Red flocks, partially soluble in CHCl <sub>3</sub>
Pt <sup>2+</sup>	.....	Acid	Violet red in aq. phase, insoluble in CHCl <sub>3</sub> ; green in CCl <sub>4</sub>
Cd	Keto-CdDz <sub>2</sub>	Strongly alkaline (5% NaOH)	Red

As has been previously explained, dithizone reacts with various metals to form yellow-orange, red and violet complexes, almost all of which are soluble in chloroform and to a lesser extent in carbon tetrachloride. By shaking the chloroform or carbon tetrachloride solution of the reagent with aqueous solutions of salts of the metals, the complexes which are formed dissolve in the organic solvent, and in this way are removed from the aqueous phase. By separating the heavier organic liquid from the aqueous solution by means of a separatory funnel, the metals are completely removed from the aqueous phase.

In order to determine individual ions in the possible presence of other ions which also react with dithizone, it is necessary properly to control conditions

so as to eliminate interference. Among the factors affecting the dithizone reaction are: (1) the concentration of the reagent; (2) the relative volume of the reagent solution and the volume of the solution of the metallic salt; (3) the thoroughness with which the two immiscible liquids are shaken; (4) the valence state of the metal; (5) the presence in the solution of complex-forming substances; and (6) the acidity of the aqueous solution.

In general then, the practical methods employed for improving the selectivity of the dithizone reaction are:

- (1) Regulating the pH of the solution to be extracted.
- (2) Adding complex-forming reagents to remove interfering metals.
- (3) Oxidation or reduction of interfering metals.

(1) *Effect of pH on the selectivity of the dithizone reaction:* Various metals which react with dithizone do so at different optimum pH values of the aqueous solution. It is therefore possible to effect separations of the various metals by

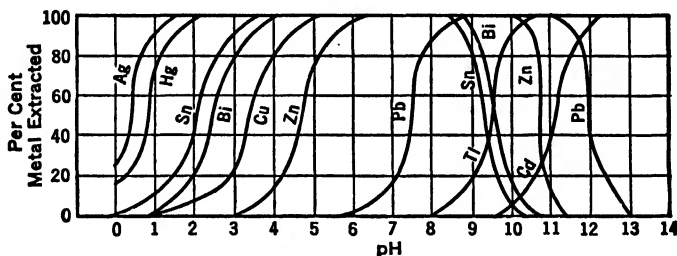


FIG. 2.—Equilibrium Curves for Some Metal Dithizonates in Chloroform.

extraction with chloroform solutions of dithizone at carefully controlled pH values of the aqueous solution. Unfortunately, the relationship of pH to the completeness of extraction of the many cations is at best fragmentary and empirical. It is known that pH governs the order in which metals are extracted from solution.<sup>11</sup> For example, the metals gold, platinum, palladium, silver, mercury, stannous tin, copper, bismuth, zinc, cobalt, nickel, lead, thallium, and cadmium, react with dithizone in immiscible solvents more or less in the above order as the reaction of the aqueous solution is progressively changed from strongly acid through weakly acid, neutral, ammoniacal and alkaline up to 5 per cent sodium hydroxide. Unfortunately, however, there are many co-extractions, and clear-cut separations are not possible in all cases. Wichmann<sup>11</sup> has constructed a series of tentative curves showing the relationship between pH of the aqueous solution and the completeness of extraction from isolated data which have been reported, but these curves cannot be regarded as complete or correctly drawn. These curves are shown in Figure 2.

Fischer<sup>16</sup> and Fischer and Leopoldi<sup>21</sup> used a green filtered solution of 0.01 g. of dithizone in 250 ml. of carbon tetrachloride, and report that the ions which give characteristic colors may be divided into groups depending upon the character of the aqueous test solution. These groups are:

I. In dilute mineral acid: copper, silver, mercury, gold and palladium.

II. In acetic acid solution: zinc, cobalt, nickel, palladium and large quantities of cadmium and tin.

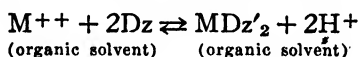
III. In sodium hydroxide solutions: silver, mercury, copper, gold, palladium, cobalt, nickel, cadmium and large quantities of zinc.

IV. In slightly alkaline solutions containing cyanide: stannous tin, thallos thallium, bismuth and lead.

V. In strongly alkaline solutions containing tartrate: cobalt, nickel and cadmium.

Ferrous iron, manganese, thallic thallium and indium react with dithizone under certain conditions, but their dithizonates are of limited stability and probably of no analytical importance.<sup>10</sup> White<sup>58</sup> states that bismuth belongs in group I of the above metals.

Recently Kolthoff and Sandell<sup>203,204</sup> have studied the reactions of dithizone with metal ions from a theoretical point of view, and have applied to them the principles of chemical equilibrium in an effort to determine the effect of pH on the completeness of extraction of the metal dithizonates. Most cations react reversibly with dithizone, according to the following equation:



in which Dz = dithizone and  $MDz'_2$  = the ketodithizonate. From this equation it is possible to derive an expression in which the extractability of the metal is shown to be a function of the pH of the aqueous solution and the concentration of dithizone.<sup>203</sup> It should be pointed out that not all metal dithizone reactions are simply reversible. For example, cobalt and nickel do not react markedly with dithizone in dilute acid solutions, but once formed in an alkaline solution they are not readily decomposed by dilute acids.

If the acidity of the solution is such that the metal is in the form of the aquo ion,  $M^{++}$ , and dithizone and the dithizonate are in non-associated forms, the following equation applies

$$\frac{[MDz'_2]_o}{[M^{++}]_w} = K \frac{[Dz]_o^2}{[H^+]_w^2}$$

in which o and w indicate the immiscible organic solvent phase and aqueous solution respectively. Concentrations are used here instead of the more exact activities. From this expression, it is readily seen that the ratio of the concentration of the dithizonate in the organic liquid to the concentration of the metal ion remaining in the aqueous solution is determined by the concentration of dithizone and the pH of the aqueous solution. It should be observed that a change in the acidity of the solution corresponding to 1 pH unit causes a change in the value of the ratio

$$\frac{[MDz'_2]_o}{[M^{++}]_w}$$

one hundred fold.

Unfortunately, the values for the equilibrium constants of the various metal dithizonates have not yet been determined. With the value for the equilibrium constant known, however, it should be possible to calculate the fraction of a metal in a solution of known pH that could be extracted by a given volume of dithizone solution of known concentration. This is illustrated by the extraction of keto cupric dithizone, for which  $K$  has been approximately determined as  $1 \times 10^{10}$  in a 1 N solution of hydrochloric acid. The following calculation is taken from the work of Sandell: 10 ml. of a 0.01 per cent solution of dithizone in carbontetrachloride is shaken with 50 ml. of 1 N hydrochloric acid containing 10% of copper. The quantity of copper remaining in the aqueous solution at equilibrium is computed as follows:

$$\frac{[\text{CuDz}'_2]_{\text{CCl}_4}}{[\text{Cu}^{++}]_{\text{H}_2\text{O}}} = K \times \frac{[\text{Dz}]_{\text{CCl}_4}^2}{[\text{H}^+]_{\text{H}_2\text{O}}^2} = 10^{10} (4 \times 10^{-4} - 3.2 \times 10^{-5})^2$$

$$= 1.35 \times 10^3$$

and

$$[\text{Cu}^{++}]_{\text{H}_2\text{O}} = \frac{[\text{CuDz}'_2]_{\text{CCl}_4}}{1350} = \frac{1.6 \times 10^{-5}}{1350} = 1.2 \times 10^{-8}$$

This corresponds to approximately 0.04% of copper in 50 ml. of the aqueous solution.

Not only is it possible to determine the quantity of metal extracted under specified conditions, but a knowledge of equilibrium constants should also make possible the prediction of conditions permitting successful separations of various metals. The separation of metals by a dithizone extraction after properly adjusting the pH of the sample solution is theoretically possible only for those metals whose dithizonates have equilibrium constants which are widely different from one another. If the acidity of the solution corresponds to 0.1-0.5 N, such metals as copper, mercury, palladium and silver may be separated from other metals. At pH 3, lead and bismuth can be separated, and in 1 N sodium hydroxide, and in the presence of citrate or tartrate to prevent precipitation of the metallic hydroxides, cadmium can be quantitatively separated from lead and zinc with a carbon tetrachloride solution of dithizone.

The various dithizonates, once formed and dissolved in different organic solvents under optimum conditions, differ in their stability toward acids. Lead, with an optimum extraction pH of 9.5, can easily be retransferred to the aqueous phase by shaking a chloroform solution of the dithizonate with dilute acid. Zinc may be retransferred in a similar manner, but a stronger acid and a more vigorous shaking is usually required. Silver, cobalt and mercury also require a rather strong acid to retransfer them to the aqueous phase.

The dithizonates of the various metals also differ from one another in their stability toward alkalies. Lead dithizonate, for example, in a chloroform solution is decomposed by an aqueous alkali in solutions at pH 11 or above. The lead either returns to the aqueous phase or is precipitated as the hydroxide. Bismuth and tin dithizonates decompose, and the metals are retransferred to the aqueous phase at a pH of 9 to 10. The critical pH governing the stability of zinc dithi-



zonate appears to be approximately 10, and that of thallium near 11. The critical pH of cadmium is 12 or above. Bismuth and tin, which are extracted with lead by dithizone, is separated from the latter metal by washing the dithizonate solution with diluted ammonium hydroxide solution at a pH of about 10.

The nature of the solvent employed also appears to exercise an effect on the action of aqueous alkalis on dithizone and the metallic dithizonates. Lead dithizonate in chloroform is more stable toward alkaline solutions than in carbon tetrachloride as is indicated by the fact that the reversion point is approximately pH 11 in chloroform and about 10 in carbon tetrachloride.<sup>11,22</sup>

From the above considerations it may be seen that it is possible not only to extract various metals from the aqueous phase through solution of their dithizonates in chloroform or carbon tetrachloride, but also to extract certain metals from the organic liquid by shaking with aqueous solutions of proper pH. This fact is often very useful in analytical procedures.

Many of the procedures which have been proposed for the determination of the metals are based upon removing the excess dithizone from the chloroform or carbon tetrachloride extract by shaking with weakly ammoniacal solutions ranging from 0.01-0.04 N, or mixtures of ammonia and cyanides and sometimes ammonium chloride. It is obvious that this treatment may result in the loss of lead through a partial decomposition of the dithizonate due to the influence of the alkaline solution.

(2) *Effect of complex-forming reagents on the selectivity of the dithizone reaction:* Proper control of pH alone is not always sufficient to effect necessary separations in analytical practice. These may be accomplished in many cases by utilizing the fact that various metallic complexes differ in their stability toward dithizone. Citrates and tartrates, for example, are used to prevent the precipitation of hydroxides or phosphates when the dithizone metals are extracted from alkaline solutions, but the presence of these complex-forming substances does not interfere with the dithizone extraction. Fischer and Leopoldi<sup>8</sup> originally proposed the use of cyanides as masking agents for certain metals. In weakly ammoniacal solutions, the cyanide complexes of most metals are stronger than the corresponding dithizonates. Lead, bismuth, stannous tin and thallium are exceptions. Consequently these four metals can be extracted from all other metals from cyanide solutions, although they cannot be separated from one another by this treatment. Fischer and co-workers<sup>23</sup> have found that potassium iodide and sodium thiosulfate may be used as discriminative complex formers in acid solutions, but not in alkaline solutions. Chloride and bromide in large excess are effective in masking silver but not mercury; iodide, however, masks both. The effect of thiosulfate and cyanide is shown by the fact that the optimum pH for the dithizone extraction of zinc which is normally 7.0 is 4.0-4.5 when the other metals are masked with sodium thiosulfate and potassium cyanide. Winkler<sup>24,25</sup> and Sandell<sup>26</sup> recommend these reagents in the determination of mercury, copper, lead and zinc with dithizone. A dilute acid solution containing a thiocyanate may be used for the extraction of copper, mercury and gold.

Thiosulfates and iodides in acid solutions may be used to decompose acid-stable dithizonates and retransfer the metals, now combined as the stronger iodide or thiosulfate complex, from the organic solvent to the aqueous phase. Winkler<sup>24,25</sup> reports that the mercury thiosulfate complex is destroyed by oxidizing the thiosulfate to the non-complex forming sulfate, and this treatment frees the mercury for a later extraction with dithizone.

Diethyldithiocarbamate is recommended for masking interference by various metals in the determination of zinc.<sup>27,163</sup> Ritchie<sup>163</sup> recommends the extraction of all possible interfering metals as carbamates and dithizonates with carbon tetrachloride from solutions that are too acid for the extraction of zinc, and then the fixation of the remaining interfering metals other than zinc with carbamate in a weakly alkaline solution. Under these conditions dithizone is almost specific for zinc. A summary of the complex-forming action of various substances in the dithizone extraction is given in Table 88.

TABLE 88.—COMPLEX-FORMING REAGENTS IN DITHIZONE REACTIONS

Conditions	Metals Reacting
Basic solutions containing citrate and tartrate.	Usually without effect
Basic solution containing cyanide.	Pb, Bi, Sn <sup>++</sup> , Tl <sup>+</sup>
Slightly acid solution containing cyanide.	Cu, Hg, Ag, Pd
Dilute acid solution containing thiocyanate.	Cu, Au, Hg
Dilute acid solution containing thiocyanate and cyanide.	Cu, Hg
Acid solution of pH 5 containing thiosulfate, and extracted with CCl <sub>4</sub> solution of dithizone.	Pd, Sn <sup>++</sup> , Zn(Cd)
Acid solution of pH 4-5 containing thiosulfate and cyanide.	Sn <sup>++</sup> , Zn
Dilute acid solution containing iodide or bromide.	Cu, Au, Pd
Dilute acid solution containing chloride.	Cu, Au, Pd, Hg

Interference in the dithizone reaction with a number of common metals under different conditions is shown in Table 89, which is taken from the work of Prodinger.<sup>205</sup>

Gutzeit<sup>5</sup> has published a review of the reactions of dithizone with a number of more common metals, and their behavior in the presence of added substances. This work is summarized in Table 90.

(3) *Effect of valence on the selectivity of the dithizone reaction:* Although altering the valence of interfering metals is of minor importance in analytical procedures, it should be noted that ferrous, stannous and platinous salts react with dithizone to form complexes, while the corresponding ferric, stannic and platinic salts do not.

**Determination of metals.** Dithizone may be used in various ways for the determination of a number of the common metals including lead, zinc, cadmium, copper, mercury and cobalt. In a number of earlier procedures, dithizone was used to extract the metal as a preliminary to a final determination with the use of methods not requiring dithizone. Many methods for determining lead,

TABLE 89.—INTERFERENCE IN THE DITHIZONE REACTION WITH METALS

Metal to be Detected	Reaction Conditions	Interfering Elements
Lead	Neutral solution KCN solution KCN solution previously oxidized	Many metals Sn, Tl None
Copper	Alkaline solution Acid solution Acid solution + KSCN Acid solution + KI Acid solution + KSCN + KCN	Ag, Au, Hg, Pt Ag, Au, Hg, Pd, Pt Au, Hg, Pt Au, Pd, Pt Hg, Pt
Silver	Alkaline solution Acid solution containing acetate	Au, Hg Au, Hg, Pd, Pt
Cadmium	Neutral solution Alkaline solution Alkaline solution + $\text{NH}_2\text{OH} \cdot \text{HCl}$	Many metals Ag, Hg, Cu Cu
Mercury	Mineral acid solution Mineral acid solution + KCN + KSCN Formic acid solution	Au, Cu, Pd Cu Au, Pd

TABLE 90.—REACTION OF DITHIZONE WITH METALS

Metal	Color	Remarks
Zinc	Purple	Stable in presence of cobalt nitrate, destroyed by potassium cyanide.
Manganese	Purple	Unstable in presence of cobalt nitrate, destroyed by potassium cyanide.
Copper	Brown	Destroyed by salts of mercury, tin, antimony, mineral acids and potassium cyanide.
Mercury	Violet	Destroyed by salts of zinc, antimony, bismuth and potassium cyanide.
Cadmium	Red	Stable in presence of potassium cyanide and cobalt nitrate.
Lead	Red	Stable in presence of potassium cyanide, destroyed by cobalt nitrate.
Cobalt	Red	Destroyed by potassium cyanide and heavy metals.

for example, have been based upon the extraction of lead, and the eventual determination of the metal by the colorimetric sulfide method.<sup>28-35</sup> After a preliminary extraction with dithizone, lead may be deposited electrolytically, and then determined iodometrically by the titration of the deposited lead dioxide.<sup>36,37</sup> Sandell and Perlich<sup>38</sup> recommend the determination of cobalt with ammonium thiocyanate and acetone after a preliminary extraction with dithizone, and Had-dock and others<sup>39-41</sup> determine bismuth colorimetrically as the iodobismuthate after a dithizone extraction. Perlman and Mensching<sup>42</sup> and Sylvester and Hughes<sup>43</sup> used dithizone to extract zinc, and then determined the zinc iodometrically with ferricyanide and potassium iodide according to the method of Lang.<sup>44,45</sup>

The red complex of metallic dithizonates may be decolorized by the destruction of the organic part of the molecule with various oxidizing agents. Hibbard <sup>46,47</sup> has used this property for determining zinc after a preliminary dithizone extraction. The zinc dithizonate is oxidized with an excess of a standard bromine solution in carbon tetrachloride, and the excess is then titrated with potassium iodide and thiosulfate. This method may also be applied to the determination of copper, lead, cobalt and cadmium.

Actual determinations employing dithizone are of three types: (1) gravimetric; (2) titrimetric; and (3) colorimetric.

(1) **Gravimetric determination.** Although insoluble metal dithizonates are formed in the reactions of dithizone with aqueous solutions of metal salts, this reaction is of little interest as a means of gravimetric determination of the metals. The precipitate formed is voluminous and retains water tenaciously during drying, and decomposes readily at a temperature near 100° C. This necessitates the ignition of the complex to the corresponding oxide, but this operation cannot be carried out simply, since dithizonates have a tendency to explode. Further, the oxide obtained by ignition is almost always contaminated with sulfide or sulfate. It should be noted also that by ignition to the oxide, the advantage of a determination form of favorable conversion factor is lost.<sup>137</sup>

(2) **Titrimetric determination.** The present methods for determinations employing dithizone are classed as colorimetric or extractive titrimetric. In the extractive titration methods, the metal is extracted from its aqueous solution at a definite pH, and in the presence of complex forming anions (when necessary), is titrated with successive portions of standardized dithizone solution. The titration is carried out in a separatory funnel with shaking between additions to establish equilibrium between the metal and reagent. The solvent layer containing the dithizonate is drawn off from time to time until the green color of the reagent is no longer changed through formation of colored dithizonates. The intense green color of the dithizone solution serves as its own indicator. This principle has been applied by Fischer and co-workers <sup>48</sup> to the determination of silver and other metals with excellent results. They recommend the titration of silver with a solution of copper dithizonate, and report that interference by other metals is less than when pure dithizone is used. Winkler <sup>24,25,185</sup> has used a similar method for determining mercury, and Wilkins and co-workers <sup>49</sup> have used a similar procedure for the determination of lead. Horwitt and Cowgill <sup>50</sup> employed a variation of this method for the determination of lead. They extracted lead with an excess of dithizone, removed the excess reagent with a very dilute cyanide solution, then decomposed the lead dithizonate to the equivalent quantity of dithizone, and titrated this with a standard lead solution.

(3) **Colorimetric determination.** The colorimetric methods have generally been regarded as among the most satisfactory for the determination of small quantities of the metals. Two techniques have been employed in the colorimetric determinations: (a) the mono-color method, and (b) the di- or mixed-color method. In the mono-color method, originally developed by Fischer

and Leopoldi<sup>8</sup> for determining lead in copper, the metal is extracted from its aqueous solution at the proper pH with an excess of the reagent in chloroform or carbon tetrachloride, and then the excess reagent is removed by treating the organic solvent with a dilute aqueous solution of ammonia, potassium cyanide or mixtures of the two. This is followed by the measurement of the color of the solution of the dithizonate. Caution must be exercised in the control of the pH of the ammonia or cyanide solution: If too high, some of the dithizonate in the organic solvent may be partially decomposed; and if too low, not all the excess reagent is removed, particularly when chloroform is employed as the solvent.

It is easier to remove dithizone from a carbon tetrachloride solution than from a chloroform solution. Clifford and Wichmann<sup>9</sup> have determined the partition coefficients for 1:200 ammonium hydroxide and carbon tetrachloride and chloroform and report the following values:

$$\frac{[Dz]_{NH_4OH}}{[Dz]_{CCl_4}} = 41 (31^\circ C.) \text{ and } \frac{[Dz]_{NH_4OH}}{[Dz]_{CHCl_3}} = 1.6 (30^\circ C.)$$

At pH 10 the coefficients are 19.4 and 0.76, respectively. Thus, by using an aqueous solution of pH 8, dithizone can be extracted from a carbon tetrachloride solution, but scarcely at all from a chloroform solution. Although dithizone is more readily removed from carbon tetrachloride than chloroform, the dithizonates are more readily decomposed in the former solvent when shaken with an aqueous alkaline solution. This may result in serious loss of the metal.

Another serious objection to the mono-color technique is the possibility of converting the keto dithizonate into the enol form by washing with an aqueous alkaline solution. This may result in a change in color of the solution of the complex. For example, there is usually a slight change in the hue of the violet solution of copper dithizonate, due to the formation of the brown enol form.

While satisfactory results have been reported for the mono-color method, the mixed-color technique is generally much to be preferred.

In applying the mono-color method, Fischer<sup>8</sup> originally converted the dithizonate to an equivalent quantity of dithizone by treating the organic extract with acids, and then matched the resulting green color with the color of standards similarly prepared. Winter and co-workers,<sup>51</sup> however, found that the red color of the metallic dithizonates could be matched with those of standards similarly prepared. The sensitivity of these methods is about 1γ.

In the di- or mixed-color method,<sup>9,52,53</sup> the metal is extracted from its aqueous solution at proper pH with an excess of the reagent in chloroform. In this case, however, the excess reagent is not removed, but is allowed to partition between the water and the organic solvent, and thus modify the color of the extracted dithizonate according to the relative quantities of the metal and reagent present. Thus, with lead, a series of colors ranging from green to red with intermediate blues, purple and crimson is obtained. This treatment avoids the error of the mono-color method—namely, the incomplete removal of the excess dithizone or the decomposition of the dithizonate with the consequent loss of

metal to the aqueous phase. The hue of the unknown solution is matched against the hues of a standard series containing known quantities of the metal. The sensitivity of the method is greatest at the ends of the series where the quantity of metal is smallest and the unchanged dithizone is greatest, and where the quantity of the metal is greatest and unchanged dithizone is smallest. This method is useful through a range of 0-200 $\gamma$  of the metal, and gives results correct within 5 per cent. It is claimed that 1 $\gamma$  of lead can be separated into 10 distinguishable parts by extracting with 5 ml. of a dilute chloroform solution of dithizone and transferring to slender 5-inch vials.

Fischer<sup>10</sup> and his associates have developed another method of mixed-color colorimetry, which is based upon duplication rather than comparison with a standard series. The mixed-color is produced in the usual manner, and then the hue of the unknown is duplicated in another vessel of the same shape and containing the same volume of dithizone and adjusted aqueous solution by alternately shaking and titrating into it a standard metal solution. The quantity of metal present is determined from the volume of standard solution used to produce the same hue as the unknown. The method is said to be very accurate for 0-10 $\gamma$  of metals. Photometric methods<sup>54,55</sup> are used to determine 1-100 $\gamma$  of lead with an error not exceeding a few per cent.

When a spectrophotometer is used to determine a metal by the mixed-color method, there are usually two possibilities in the choice of wave length: one is to measure the absorption of light by the metal complex, and the other is to measure the absorption of light by the excess dithizone remaining after the completion of the reaction with the metal. In carbon tetrachloride, the approximate wave lengths ( $m\mu$ ) of maximum absorption by dithizone and the keto dithizonates of a number of common metals have been determined, and are given in Table 91.

TABLE 91.—WAVE LENGTHS OF MAXIMUM ABSORPTION OF DITHIZONE AND KETO DITHIZONATES OF COMMON METALS IN  $CCl_4$

Metal	Wave Length in $m\mu$
Dithizone .....	620, 450 (secondary)
Bismuth .....	504
Cadmium .....	520
Cobalt .....	Ca. 560
Copper (II) .....	510
Lead .....	525
Mercury (II) .....	530
Silver .....	460
Thallium (I) .....	500
Tin (II) .....	508
Zinc .....	535

It may be seen from the above discussion that the usefulness of dithizone as a reagent is somewhat limited by its lack of specificity, since with the exception of mercury and silver most dithizonates are red and indistinguishable.

They do, however, differ from one another in spectral character and optical methods may therefore offer some means of distinguishing one dithizonate from another.<sup>56,57</sup> Clifford has succeeded in accomplishing this in the determination of lead by using normal and auxiliary wave lengths or filters. The maximum absorption of red dithizonates occurs at wave lengths of 500-560  $m\mu$ .<sup>15</sup> These maxima are so close together that all red dithizonates absorb to some degree at any of these wave lengths, and the differentiation at any selected wave length is difficult or impossible. It has been observed, however, that the definite relationship between absorption of a given quantity of dithizonate at different wave lengths is disturbed by the presence of metal impurities with different spectral characteristics. Auxiliary wave lengths or filters may be so chosen that the disturbing effects of any interfering metal in any given dithizonate will be at a maximum. Thus, if data obtained for normal and auxiliary filters are characteristic of lead dithizonate, the final lead dithizonate obtained is pure, or contains bismuth and tin in quantities not to exceed a few per cent of the lead determined. If, on the other hand, satisfactory agreement is not obtained, serious quantities of bismuth and/or tin contamination is indicated, and a repetition of the lead separation should be carried out.

A number of excellent reviews have appeared in the literature covering more or less generally the applications of dithizone to problems of chemical analysis.<sup>9-11,58-61</sup> These papers contain much useful information.

**Detection of lead.** Dithizone dissolves in chloroform or carbon tetrachloride with the formation of an intensely green colored solution. The tinctorial power of this reagent is very great; one part of the compound gives a perceptible green color with 40,000,000 parts of solution. When the green chloroform solution is shaken with solutions containing lead, the red lead dithizonate which is formed dissolves in the chloroform layer to produce colors ranging from violet to red. So many factors influence the development of the color, that it is difficult to state accurately the sensitivity of the test unless the conditions are specified exactly. In general about 2 $\gamma$  of lead can be detected by shaking 1 ml. of a 0.1 per cent chloroform solution of dithizone with 10 ml. of the aqueous solution to be tested. The delicacy of this test may be increased by approximately 100 times by the use of a microtechnique using a spot plate.<sup>58</sup>

Although lead reacts with many metals to give colored complexes, by carrying out the test with an ammoniacal potassium cyanide solution of the material to be tested, fairly large quantities of silver, copper, nickel, zinc, cadmium, antimony, bismuth and arsenic do not interfere. Tin, thallium and large quantities of bismuth and cadmium interfere and must be separated by appropriate means.<sup>79</sup>

By shaking violently one drop of a neutral test solution with a drop of a solution containing 1-2 mg. of dithizone in 100 ml. of chloroform, as little as 0.04 $\gamma$  of lead can be detected. In a 2 per cent solution of ammonia, only 0.3 $\gamma$  of lead can be detected, and in a 5 per cent potassium cyanide solution, 0.1 $\gamma$  of lead gives the test.<sup>62</sup> Various investigators<sup>5,63-66,191</sup> have reported the use of dithizone for the detection of small quantities of lead. Bohnenkamp and Linneweh<sup>67</sup> have used dithizone for the detection of lead in urine in poisoning cases.

They report that 0.1 $\gamma$  of lead is detectable and that the method is superior to a spectrographic detection.

Llacer <sup>201</sup> has used a 2 per cent solution of dithizone in pyridine as a reagent for the microchemical detection of lead. The test is applied in a dilute nitric acid solution of pH 0.5-1.0. The microcrystals are detectable even in the presence of silver and mercury.

**Determination of lead.** One of the steps in any procedure for the determination of lead with dithizone consists of extracting the metal with a chloroform or carbon tetrachloride solution of the organic reagent. Consequently, the accuracy of any such determination depends upon the completeness of the extraction of lead, and upon its separation from other metals which give a similar color reaction with dithizone. The extraction has been found to depend upon the control of the volume of the solvent and the aqueous solution, the concentration of dithizone in the solvent phase, and the pH of the solution containing the lead.

Clifford and Wichmann <sup>9</sup> have studied the effect of pH upon the extraction of lead with dithizone, and also have observed the effect of different quantities of dithizone upon the extraction. These results are shown in Table 92.

TABLE 92.—RECOVERY OF LEAD WITH EXCESS DITHIZONE  
AT DIFFERENT pH

pH	25% Excess of Dithizone		50% Excess of Dithizone	
	mg. of Lead	Per Cent Recovered	mg. of Lead	% Recovered
5.0	.....	....	0.0004	0.16
5.5	.....	....	0.0015	0.60
6.0	0.0016	0.64	0.0099	4.0
7.0	0.019	7.6	0.59	23.6
8.0	0.198	79.0	0.239	96.0
8.5	0.242	97.0	0.249	100
9.0	0.249	100	....	....
11.0	0.249	100	0.248	99.0
12.0	0.233	93.0	0.239	95.0

Biefeld and Patrick <sup>14</sup> have also studied the effect of pH upon the extraction of lead, and in addition have studied the effect of various anions and the amount of reagent used in lead determinations with dithizone. The partition of dithizone between chloroform and the aqueous layers at different pH is shown in Figure 3:

From this it will be seen that a suitable correction must be applied for the transfer of dithizone to the aqueous layer at pH values above 8 when the mixed-color technique is used.

Biefeld and Patrick <sup>14</sup> have extended the work of Clifford and Wichmann <sup>9</sup> and have studied the effect of pH upon the extraction of lead of varying quan-



tities with dithizone from solutions containing various anions. These results are shown in Figures 4, 5 and 6.

Citric or tartaric acid is used in the solution to be extracted to prevent the precipitation of metals as hydroxides or phosphates. Biefeld and Patrick<sup>14</sup> recommended that citric acid not be used if some other means can be found. Tartrates, provided they function in the same manner as citrates, are satisfactory.

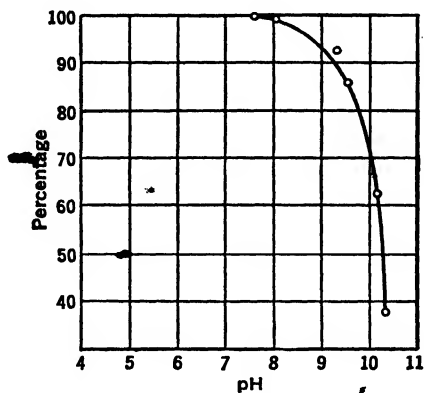


FIG. 3.—Effect of pH upon the Retention of Dithizone by the Chloroform Layer.

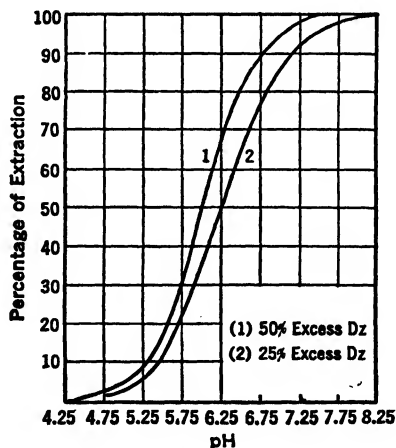


FIG. 4.—Effect of pH and Excess Dithizone upon Lead Extraction from Acetate Solutions.

Kety<sup>68</sup> states that citrate forms a complex with lead. Ammonia-cyanide solutions acidified with hydrochloric acid are readily extracted, and show the greatest pH range for complete extraction. The disadvantage in the use of this medium, however, depends upon the highly poisonous character of the hydrogen cyanide which is formed if the mixture is overacidified. The use of the acetate ion as a complex former does not interfere markedly in the dithizone

extraction. The use of acetate offers the further advantage that the pH is very easily regulated to almost any desired value. High pH values are to be avoided whenever possible in lead determinations because of partitioning of dithizone to the aqueous phase. For cyanide-ammonia-citrate solutions, a pH of 9.5 or greater is required for complete extraction. With cyanide-ammonia-

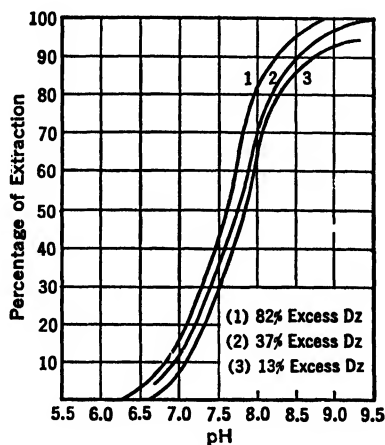


FIG. 5.—Effect of pH and Excess Dithizone upon Lead Extraction from Cyanide-Citrate Solutions.

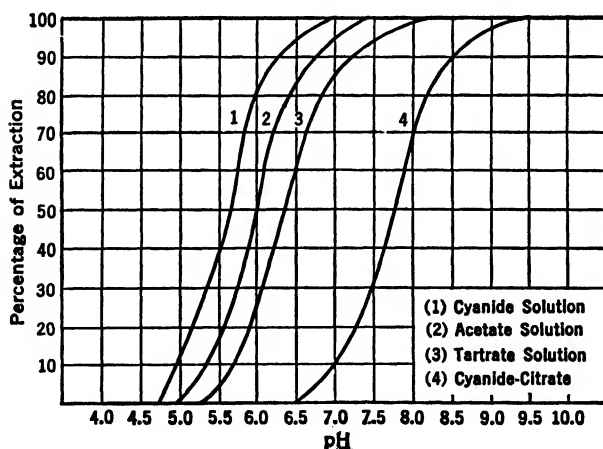


FIG. 6.—Effect of Anions upon Lead Extractions, Using 50 Per Cent Excess of Dithizone.

hydrochloric acid solutions, extraction is complete at values greater than 7.0.

If lead is extracted from an alkaline solution, substances capable of forming a precipitate which will occlude lead must be absent. The extraction fails in the presence of much calcium or magnesium and phosphorus, since the phosphates of these metals are only slightly soluble in an ammoniacal citrate solution and carry down lead strongly. Stannic acid also carries down lead.

**Interference with the lead determination.** Since in addition to lead, stannous tin, thallos thallium and bismuth are extracted by a chloroform or carbon tetrachloride solution of dithizone from a slightly alkaline solution containing cyanide, these metals may interfere with the lead determination. Consequently special methods may be required for the estimation of lead in the presence of any of these metals.

(a) *Interference by tin:* Since stannic tin is not extracted with dithizone in the presence of potassium cyanide, various investigators<sup>50,55</sup> recommend the oxidation of any stannous tin to the stannic condition before carrying out the extraction. Wichmann and Clifford<sup>69</sup> state that stannic tin is not extracted with dithizone in presence of potassium cyanide but under the conditions used in the extraction, some of the stannic tin is slowly reduced. They recommend separating tin electrolytically or by volatilizing as stannic bromide.<sup>56,60</sup> Horwitt and Cowgill<sup>50</sup> state that small amounts of stannous tin can be separated from a chloroform solution of lead dithizonate by shaking with 0.5 per cent potassium cyanide. Lang<sup>55</sup> recommends eliminating tin interference by oxidizing to insoluble metastannic acid which is not extracted. He further states that reduction to stannous condition does not occur. Stannic acid may, however, carry down lead. Clifford<sup>70</sup> recommends the use of cupferron for eliminating interference by iron and tin. Iron, tin and about 80 per cent of the bismuth in 100 ml. of an acid solution are precipitated with cupferron and then extracted with ether or chloroform. This treatment leaves the soluble cupferrides, including lead, in the aqueous phase. The lead is freed from the cupferron complex with bromine, and is later extracted from an ammoniacal solution, separated from bismuth and then determined.

(b) *Interference by bismuth:* Willoughby and co-workers<sup>71</sup> have reported that bismuth and lead can be separated by extracting the aqueous solution with dithizone at a pH of 2. At this pH no lead enters the dithizone phase, but the bismuth is slowly extracted, and may be completely removed by repeated extractions. They recommend the following procedure:

**Procedure.** To the nitric acid solution containing lead and bismuth, add 2 drops of *m*-cresol purple, and adjust the solution to pH 2 by the addition of 5 per cent ammonium hydroxide solution. The total volume should be approximately 25-35 ml. Then extract with 25 ml. of a solution prepared by dissolving 40 mg. of dithizone in a liter of chloroform. Shake vigorously for two minutes. Repeat this treatment twice with 5 minutes shaking until finally a colorless extract is obtained, showing that all bismuth has been removed.

Wash the aqueous solution with chloroform to remove any dithizone, and then add 2-3 drops of a 0.02 per cent solution of phenol red and 2 ml. of 10 per cent potassium cyanide solution. Adjust the pH to 7.5 with nitric acid and extract with dithizone in the usual manner.

Various investigators<sup>51,72,78</sup> have recommended separating bismuth by extracting a dithizone mixture of the alkali cyanides. Clifford and Wichmann,<sup>9</sup> state that by this treatment some of the bismuth is also extracted, and this is

confirmed by Horwitt and Cowgill.<sup>50</sup> These authors state that some bismuth is extracted if 1 per cent of potassium cyanide is present, but say that the loss is negligible with only 0.5 per cent potassium cyanide. They recommend the method of Willoughby and co-workers<sup>71</sup> with large quantities, but prefer the extraction at a pH of 3-3.5 rather than 2.0. Shiels<sup>74</sup> recommends 3.5 as the best pH for the lead-bismuth separation, and Fischer and Leopoldi<sup>75</sup> make the separation at pH 3. Reith and van Dijk<sup>76</sup> have determined lead in the presence of thallium and bismuth, and have separated lead and bismuth by extracting with dithizone at a pH of 4.0. Wichmann<sup>56,69</sup> has separated bismuth prior to the lead determination by extracting bismuth iodide with ethyl acetate.

Bismuth is not a common constituent of biological materials, and yet it occurs with sufficient frequency that its possible presence can not be neglected in making lead determinations in materials of this type. In many of the older procedures, a time-consuming bismuth test was necessary in order that the analysis might be regarded as specific. Bambach and Burkey<sup>77</sup> have proposed a method of lead-bismuth separation in which the preliminary bismuth test is eliminated. If instead of using dilute acid to strip the metals from the dithizone solution, an aqueous solution regulated to pH 3.4 is used, lead and bismuth are separated, and no subsequent bismuth or lead test is necessary. The pH in this separation must not differ markedly from 3.4, and in order to prevent entrained salts from changing this value, the solution must be suitably buffered.

The following procedure, which is taken directly from the published work of Bambach and Burkey,<sup>77</sup> is given to illustrate the method used in determining lead in materials which may contain small quantities of bismuth. Since the majority of lead determinations employing dithizone are carried out on biological materials, the methods used by Bambach and Burkey<sup>77</sup> for preparing samples of various materials for analysis are also given: \*

**Preparation of samples.** (a) *Urine*: Add concentrated nitric acid (10 per cent of the sample volume) to the measured sample; evaporate to dryness on a hot plate or steam bath, and ignite at 500° C. in a silica or pyrex evaporating dish. Moisten the ash with nitric acid, dry, and ignite for a few minutes until it is white; then dissolve in dilute nitric acid. The sample is ready for analysis. Filtration is not necessary.

(b) *Feces*: Dry the sample on a hot plate or steam bath to constant weight in a tared silica or pyrex dish, place on an electric heater at a low red heat until all volatile matter which would otherwise flame in the muffle furnace is driven off, and ignite at 500° C. Weigh the ash and dissolve in a mixture of hydrochloric and nitric acids. The sample is ready for analysis. Filtration is not necessary and should not be employed, since the removal of silica in appreciable quantities will result in the loss of entrained lead unless the precipitate is very thoroughly washed.

(c) *Foods*: Digest the weighed sample of mixed food with concentrated nitric acid on a hot plate or steam-bath until all lumps have disappeared. This

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may require more than a week, with repeated additions of acid. If a food homogenizer, such as a Waring Blendor, is used, the time may be materially shortened, especially since aliquants may then be employed. (Unless sample can be made homogeneous by this or some similar method, the entire sample must be analyzed.) Evaporate the sample to a sirupy consistency, transfer to a silica or pyrex evaporating dish, and add concentrated sulfuric acid (15 ml. for an average day's mixed food). Then place the dish on an electric heater at a low red heat and treat as described under "Feces."

(d) *Tissues*: In general, the weighed sample is treated in the same way as a sample of mixed food.

(e) *Blood*: Transfer the sample to a tared silica or pyrex evaporating dish and weigh, and then add concentrated nitric acid (5 to 10 ml. per 10 g. of blood). Evaporate the mixture to dryness on a hot plate or steam-bath, place on an electric heater at a low red heat, and ignite in a muffle furnace at 500° C. Add a few milliliters of hydrochloric acid to the ash, then nitric acid, and heat the dish on the hot plate until the sample is dissolved. It is then ready for analysis.

**Reagents and Apparatus.** *Ammonium citrate solution*: Dissolve 400 g. of citric acid in water and add sufficient reagent ammonium hydroxide to make the solution alkaline to phenol red. Dilute the solution to 1 liter with water and purify by shaking repeatedly with portions of a solution of dithizone in chloroform until the dithizone retains its original green color.

*Distilled ammonium hydroxide*: Distill reagent ammonium hydroxide into double-distilled water which is chilled in an ice bath.

*Hydroxylamine hydrochloride solution*: Dissolve 20 g. of hydroxylamine hydrochloride in sufficient water to make about 65 ml., and add a few drops of *m*-cresol purple indicator solution. Next add concentrated ammonium hydroxide until a yellow color results. Add sodium diethyldithiocarbamate in water (an approximately 4 per cent solution) in sufficient quantity to combine with all the lead (and most other metals) present and to leave a considerable excess. After a few minutes completely extract the organo-metallic complexes and the excess reagent with chloroform. The absence of a yellow color in the chloroform when a portion of the chloroform extract is shaken with a dilute solution of a copper salt indicates when this point is reached. Then add distilled hydrochloric acid to the hydroxylamine hydrochloride solution until the indicator turns pink, and add double-distilled water to make the final volume 100 ml. It is not necessary to filter the solution.

*Potassium cyanide solution*: Shake repeatedly a practically saturated solution containing 50 g. of potassium cyanide in sufficient water to make 100 ml. with portions of dithizone in chloroform (30 mg. per liter) until the lead is removed. Part of the dithizone dissolves in the aqueous phase, but enough remains in the chloroform to color it and to indicate when the lead has been completely extracted. Most of the dithizone in the aqueous phase can be removed, if desired,

by repeated extractions with pure chloroform. Then dilute the strong potassium cyanide solution with double-distilled water to the proper strength (10 g. per 100 ml.). It is not necessary to filter the solution. (If instead of the concentrated solution, the final one is shaken with dithizone in chloroform in an attempt to delead it, the increased alkalinity of this dilute solution causes the removal of all the excess dithizone from the chloroform and renders the complete extraction of the lead more difficult.)

*Dithizone extraction solution:* Shake 1 liter of chloroform with 100 ml. of water containing about 0.5 g. of hydroxylamine hydrochloride, which has been made alkaline to phenol red with ammonium hydroxide. Drain off the chloroform and dissolve in it 30 mg. of dithizone. Add approximately 5 ml. of alcohol to the solution if part of it is to be kept for several days. Filtration is not necessary. Shake the quantity of dithizone solution to be used for one day with about 100 ml. of dilute nitric acid (1 ml. per 100 ml. of solution) just before use.

*Standard dithizone solutions:* Prepare these solutions from distilled chloroform which has been treated with hydroxylamine, as in the instructions for the dithizone extraction solution. In this case, however, filter the chloroform through a dry paper into a glass-stoppered pyrex bottle, which is wrapped with heavy paper or kept in a wooden box to protect it from light. Dissolve the proper amount of dithizone (5 mg. per liter for the 0- to 10-microgram range, 10 mg. per liter for the 0- to 50-microgram range, and 20 mg. per liter for the 0- to 100-microgram range) in the chloroform, add absolute alcohol (5 ml. per liter), and the solution is ready for standardization. It should be kept in a refrigerator.

*Ammonia-cyanide mixture:* Each liter of the mixture contains 20 g. of potassium cyanide and 150 ml. of distilled ammonium hydroxide (specific gravity 0.9), or its equivalent; dilute to volume with double-distilled water. This solution should be kept in a cool place.

*Buffer solution, pH 3.4:* Dilute reagent nitric acid (9.1 ml.) to approximately 500 ml. with double-distilled water in a 1-liter volumetric flask, add bromophenol blue indicator, and adjust the pH to 3.4 with distilled ammonium hydroxide. Then add 50 ml. of Clark and Lubs potassium acid phthalate-hydrochloric acid buffer, pH 3.4 double strength (50 ml. of 0.2 M potassium acid phthalate and 9.95 ml. of 0.2 M hydrochloric acid, per 100 ml.). Dilute the solution to 1 liter with double-distilled water.

*Apparatus:* Pyrex glassware should be used throughout; containers should all be glass-stoppered. The extractions are most conveniently carried out in Squibb-type separatory funnels, 150-ml. capacity, graduated at 5- and 10-ml. intervals to 100 ml., with the aid of rotary funnel racks.<sup>116</sup> White vaseline is used to grease the stopcocks, since it is practically lead-free.

Any photometer which can be used with the cells described is usually satisfactory for this procedure. A glass filter with maximum transmission at 510

millimicrons is suitable. The neutral wedge photometer described by Clifford and Wichmann<sup>9</sup> was originally employed in this work.

**Isolation of lead.** Pour approximately 15 ml. of the ammonium citrate solution into each of the lower funnels, using the graduation marks on the funnels as a guide. Next add the proper aliquants of the prepared samples (equivalent to 50 to 200 ml. of urine, 0.1 to 0.5 g. of fecal ash, 5 to 20 g. of blood, or one-tenth of a normal day's food), together with 5 ml. of potassium cyanide solution and 1 ml. of hydroxylamine hydrochloride solution, and make the mixtures alkaline to phenol red with distilled ammonium hydroxide. In rare instances the solutions will become very cloudy upon being made alkaline, because of the presence of an unusually large quantity of calcium phosphate; in such a case, add sufficient ammonium citrate solution to dissolve the precipitate.

Start the extraction of lead with 5 ml. of dithizone extraction solution and note the color in order that the proper standard dithizone solution may be chosen in the final lead estimation. (Usually the lead is not extracted quantitatively with each portion of dithizone solution because of the various salts present. Instead of 50 micrograms of lead, which is the theoretical equivalent of the dithizone, only 40 micrograms will be extracted, as a rule, by each 5 ml. When the quantity of lead present is less than 10 micrograms, this is recognized by the distinctive greenish-blue color of the dithizone.)

Add another 5-ml. portion of dithizone solution, using the graduation marks on the funnels as a guide. Before draining this combined 10 ml. solution into the other funnel, note its color, for this should indicate whether the quantity of lead present is greater than 50 micrograms, or greater than 100 micrograms. Then continue the extraction with successive 5-ml. portions of dithizone solution, noting the color of each portion and draining each before adding the next, until the lead is completely extracted.

Wash the combined dithizone extracts with approximately 50 ml. of double-distilled water, and wash the water with 5 ml. of distilled chloroform. This chloroform wash should be green in color; if it is not, the presence of lead or zinc is indicated. Then add a drop of potassium cyanide solution to the water and again shake the funnel; if the chloroform phase does not become green, wash the water at least once with dithizone extraction solution. Add all chloroform washings to the dithizone extract and discard the water. Strip the lead from the dithizone extract by shaking with 50 ml. of buffer solution (pH 3.4); if the dithizone solution does not return to its original green color, bismuth is present. Drain the dithizone solution from the funnel, and if the presence of bismuth has been indicated, shake the buffer solution with one 5-ml. portion of dithizone solution. After this is drained out, add 5 ml. of distilled chloroform and shake the mixture.

If the sample contains more than 100 micrograms of lead, as indicated by the color of the separate portions of dithizone extraction solution noted early in the lead isolation step, discard part of the buffer solution containing the lead before adding the 5 ml. of distilled chloroform. The quantity discarded should be sufficient to reduce the lead content to less than 100 micrograms; this is conveniently done by using the graduation marks on the funnel. Make up the

volume to 50 ml. by adding more buffer solution, and add the chloroform as indicated above.

Allow the funnel to stand unstoppered until the drop of chloroform floating on the surface of the aqueous phase has evaporated, and draw off the 5 ml. of chloroform as completely as possible without allowing the water to enter the bore of the stopcock.

**Final estimation of lead.** In the following portion of the procedure, do not allow direct sunlight to strike the solutions.

Add the proper standard dithizone solution (10 ml. of the 0- to 10-microgram solution, or 25 ml. of the 0- to 50- or 0- to 100-microgram solution) to the funnel containing the lead in 50 ml. of buffer solution; add 7 ml. of ammonia-cyanide mixture and immediately shake the funnel for 1 minute. Do not release the pressure which develops through the stopcock, but instead, lift the stopper in order to avoid blowing water into the funnel stem. If a number of analyses are being run, develop the mixed color in the whole series and take photometric readings one after the other.

Use part of the dithizone solution (2 ml. of the 0- to 10-microgram solution, or 10 ml. of the 0- to 50- or 0- to 100-microgram solution) to flush the stem of the funnel; dry the end of the funnel stem, and allow the solution to run directly into the proper cell for the photometric reading. Use the 0- to 10-microgram solution with a 5-cm. (2 inch) cell, the 0- to 50-microgram solution with a 2.5 cm. (1 inch) cell, and the 0- to 100-microgram solution with a 1.25-cm. (0.5 inch) cell. The cells are cylindrical, with optically plane ends and have an internal diameter of about 14 mm. Since the 0- to 10-microgram cell holds the entire 8 ml. remaining in the funnel, it cannot be rinsed with part of the dithizone solution, but must be cleaned and dried with pure acetone after each sample. The other two cells, however, can be rinsed with dithizone solution at least twice, and it is rarely necessary to wash or dry them between samples.

Refer the photometric readings to calibration curves made for each standard solution in the following way:

Prepare a standard lead nitrate solution by dissolving recrystallized lead nitrate in 1 per cent nitric acid, so that each milliliter contains 1 mg. of lead. From this solution, make two dilutions in 1 per cent nitric acid, one containing 10 micrograms of lead per milliliter, and the other 1 microgram per milliliter. All these solutions will keep indefinitely in glass-stoppered pyrex containers.

Prepare a standard lead solution in the proper buffer by taking a measured quantity of the desired standard lead solution, bringing it to pH 3.4 by addition of dilute distilled ammonium hydroxide, adding the proper amount of the Clark and Lubs buffer mentioned above, and diluting the mixture to a known volume. This solution should be made fresh each time it is used.

Add measured quantities of this standard lead solution to clean separatory funnels, bring the volume in each funnel to 50 ml. with the pH 3.4 buffer solution, and add the dithizone solution to be standardized. Carry out color development and photometric readings as in the final estimation of lead. From these readings, prepare a standard calibration curve.



(c) *Interference by thallium*: Since thallous thallium is extracted with lead by dithizone from solutions containing potassium cyanide, special precaution must be taken to prevent interference by this element. According to Clifford,<sup>18</sup> the separation is made from solution of pH 6.0-6.4. Lead is extracted under these conditions, while thallium remains in the aqueous phase. By extracting with three 20-ml. portions of a solution of 100 mg. of dithizone in a liter of chloroform, 50 mg. of lead can be separated from 1 mg. of thallium. Fischer and Leopoldi<sup>75</sup> state that at a pH of 9, 0.5% of lead can be detected in the presence of 12 mg. of thallous thallium. In separating lead from thallium in the presence of potassium cyanide, these investigators take advantage of the fact that lead dithizonate is formed before the analogous thallium compound. Reith and van Dijk<sup>76</sup> have described a method for the determination of lead in the presence of thallium and bismuth. In this procedure no special step is necessary to eliminate interference by thallium, since the extraction is carried out at a pH of 7.5, at which pH they claim that as much as 1000% of thallium scarcely gives a perceptible reaction with dithizone. Fischer and Leopoldi<sup>8</sup> recommend the elimination of interference from thallium by oxidizing to the trivalent state.

(d) *Interference by iron*: Ferric iron may interfere in the lead determination with dithizone by oxidizing the latter to a colored compound.<sup>20,78</sup> Further, when large quantities of iron are present in samples to be analyzed for lead colorimetrically with dithizone, a fading of the color occurs due to oxidation of the reagent. Wilkins<sup>49</sup> resorted to a preliminary dithizone extraction in which the partial destruction of the reagent by ferric iron was not important. Thomsett and Anderson<sup>72</sup> avoided iron interference by a preliminary extraction with sodium diethyldithiocarbamate. Fischer and Leopoldi<sup>79,80</sup> suggested the addition of hydroxylamine hydrochloride to prevent the oxidation of dithizone. This is effective if not more than 1 mg. of iron is present. With greater quantities of iron, the authors recommend the transformation of the ferric iron to the tartrate complex, which does not oxidize the lead-dithizone complex. Harrold and co-workers<sup>118</sup> have used hydroxylamine hydrochloride to prevent interference by iron in the determination of lead in air. Iron may also be eliminated prior to the lead determination by treating the solution to be analyzed with cupferron.<sup>81</sup>

(e) *Interference by copper*: Traces of copper may catalyze the oxidation of dithizone by certain substances, but such an effect can be prevented by adding hydroxylamine hydrochloride and boiling the mixture.<sup>75</sup>

(f) *Interference by indium*: Indium appears to be extracted under the same conditions as lead, bismuth, tin, and thallium, and may therefore interfere with the lead test.<sup>18</sup>

**Methods for the determination of lead. Preliminary Extractions:** In many of the older methods which have been proposed for the determination of lead, the metal is extracted with dithizone and then determined with the aid of other reagents, after destroying the reagent by oxidation or freeing the metal from the dithizonate by extraction with acids. The colorimetric sulfide estimation has been one of the more frequently used methods for lead determination.<sup>28-35</sup> This procedure has been particularly recommended by Allport and Skrimshire<sup>28-30</sup>

for the determination of small quantities of lead in organic materials such as drugs, dyes, etc.

**Procedure.** Heat a suitable quantity of the dye or other organic material with sulfuric and nitric acids, and then free the residue from nitric acid by diluting with water and evaporating to the appearance of white fumes. Cool, dilute with water, add 2 g. of citric acid and then make alkaline with ammonium hydroxide. Finally add 1 ml. of 10 per cent potassium cyanide. Then extract the cooled solution, which should have a volume of 100-150 ml., three times in a separatory funnel by shaking vigorously with a 0.1 per cent solution of dithizone in chloroform. Use 10 ml. of the dithizone reagent for the first extraction and 5 ml. for the second and third extractions. If after the third extraction the chloroform solution is bright red, continue the extraction with additional 5-ml. portions of the reagent until the red color is no longer obtained. Wash each extract with 10 ml. of water contained in a second separatory funnel, transfer to a flask, and evaporate the chloroform. Add 0.5 ml. of sulfuric acid to the residue and destroy the organic matter by heating and adding to the hot sulfuric acid solution a few drops of nitric acid. Dilute the residue with water, add 2 g. of ammonium acetate and make alkaline with ammonium hydroxide. Add 1 ml. of 10 per cent potassium cyanide solution, 0.1 ml. of 10 per cent sodium sulfide solution and match the resulting color with that of standard lead solutions similarly prepared. If more than 0.1 mg. of lead is present, a suitable aliquot should be used for the formation of lead sulfide.

Lead may be deposited electrolytically after extraction with dithizone and the lead peroxide, which is formed, determined iodometrically.<sup>86,87</sup> In methods used by Loughrey<sup>82</sup> and Fairhall and Keenan,<sup>83</sup> lead is extracted with dithizone, and after the lead dithizonate is decomposed, the lead is redissolved with nitric acid, neutralized, and precipitated as the chromate. This is dissolved in hydrochloric acid and the solution is treated with potassium iodide, and then titrated with sodium thiosulfate with a few drops of carbon disulfide as the indicator.

Heller and co-workers<sup>84</sup> extract lead and other metals from water prior to a polarographic determination by the method of Heyrovsky.<sup>85</sup> Menard<sup>86</sup> has extracted lead with dithizone and determined lead in the extract with the dropping mercury electrode according to the method of Feicht and co-workers.<sup>87</sup>

**Colorimetric determination.** The most important of the recent methods for the determination of lead with dithizone are based on colorimetric principles. A number of colorimetric methods have been proposed, but in general these are simply variations of the two basic techniques, the mono-color method, and the mixed-color method. Regardless of the method employed, the first step in the colorimetric determination of lead is the isolation of the metal from the sample. The following method, which is taken from the work of Sandell,<sup>204</sup> may be regarded as similar to and typical of the many methods described by other investigators:

**Reagents.** *Dithizone reagent:* Dissolve 50 mg. of dithizone in 1 liter of chloroform. Protect from light.

**Ammonium citrate solution:** Dissolve 50 g. of ammonium citrate in 100 ml. of water. Adjust the pH to 8.5-9 with ammonium hydroxide, and shake with several successive portions of the dithizone solution until all lead is removed. Remove any excess dithizone by shaking the solution with a little chloroform, and drawing off the latter.

**Potassium cyanide solution:** Prepare an approximately saturated solution of potassium cyanide by dissolving 50 g. of the salt in sufficient water to make 100 ml. of solution, and then shake with several successive portions of the dithizone solution until all lead is removed. This point is indicated by a pure green color in the final chloroform extract. Remove the excess dithizone from the aqueous layer by extracting with a little chloroform, and then dilute with water to a concentration of 10 per cent.

**Hydroxylamine hydrochloride<sup>a</sup> solution:** Add 20 g. of hydroxylamine hydrochloride to 65 ml. of water containing a few drops of *m*-cresol purple, and then add ammonium hydroxide dropwise until a yellow color appears. Add 1 ml. of a 5 per cent solution of sodium diethyldithiocarbamate, and shake the solution with successive portions of chloroform until the metal diethyldithiocarbamates and the excess reagent are removed. Completeness of extraction of the reagent is indicated when the chloroform extract yields no yellow color when shaken with a dilute solution of copper sulfate. Add hydrochloric acid to the hydroxylamine hydrochloride solution until the indicator turns pink, and then dilute with water to 100 ml.

**Isolation of lead.** Prepare the sample by suitable means, and transfer the sample solution, or an aliquot part of it, containing 1-100 $\gamma$  of lead to a glass-stoppered separatory funnel. Add 15 ml. of the ammonium citrate solution and 1 ml. of the hydroxylamine hydrochloride solution, and then a few drops of thymol blue indicator. Add pure ammonium hydroxide dropwise until the solution is basic, and then add 5 ml., or more if necessary, of the potassium cyanide solution. Adjust the pH of the solution to 8.5-9, which is indicated by the greenish color of the indicator. Add 2-5 ml. of the dithizone solution and shake 15 seconds. If the amount of lead present is unknown, the approximate concentration may be determined by adding the dithizone in increments of 1 ml., with shaking after each addition, until the color begins to differ from the pure red of lead dithizonate. One ml. of pure 0.005 per cent dithizone solution is equivalent to approximately 20 $\gamma$  of lead. This information may be of value in the final determination.

Draw off the chloroform layer into a second separatory funnel, and again extract the sample solution with another 2-5 ml. of dithizone solution. Combine this extract with the first, and repeat the extraction if necessary. Extraction is complete when the last extract shows no mixed color. Add 10-20 ml. of water to the combined extracts, shake, and draw off the chloroform into a separatory funnel. Extract the aqueous solution with 1-2 ml. of dithizone, and add to the main dithizone extract.

Shake the combined chloroform extracts with 2 successive 25-ml. portions of 1:100 nitric acid. Combine the aqueous extracts in a separatory funnel, and

remove any remaining dithizone solution by shaking with a little chloroform, and then drawing off the latter. Swirl the solution in the funnel to collect the droplets of chloroform into one drop, and draw this off, leaving the bore of the stopcock filled with chloroform. If any chloroform remains on the surface of the liquid, remove the stopper from the funnel until it has evaporated. Dry the stem of the funnel with a roll of filter paper. The resulting aqueous solution is now ready for the final determination by any of the usual colorimetric methods employing dithizone.

For the actual determination, either the mono-color method or the mixed color method can be used. The details of these methods are discussed in the following sections.

**Determination of lead by the mixed-color method.** In the mixed-color method,<sup>9,52,53</sup> lead is extracted from its aqueous solution at an optimum pH with an excess of dithizone in chloroform. Using this technique, the excess reagent is not removed, but is allowed to partition between the water and the solvent and thus to modify the color of the extracted dithizonate according to the relative quantity of lead and dithizone. Thus a series of colors ranging from green to red may be formed with intermediate blue, purple and crimson hues. Carbon tetrachloride is unsuited for mixed-color determinations, as it allows the excess reagent to partition too readily into the aqueous phase. If the extraction is carried out under definite conditions of volume and strength of the dithizone solution, and volume and pH of the aqueous phase, the mixed-color obtained is definite and reproducible; and, provided an excess of dithizone is used, depends only upon the quantity of lead present. This method avoids the errors of the mono-color procedure, which result from incomplete removal of dithizone and the solubility of lead dithizonate in alkaline wash solutions. This is accomplished by leaving in the excess dithizone, and carrying out the extraction at a pH at which there is no loss of lead. The optimum of pH appears to be 9.5-10.<sup>9</sup> This is adjusted as follows: Dissolve the lead in a definite volume of solution and of definite acid strength, and then make ammoniacal with a definite volume of ammonia-cyanide solution of suitable strength until the proper pH is attained.

The concentration of lead dithizonate in the organic solvent originally having a fixed concentration of dithizone may be determined photometrically by several methods:<sup>52,54,55,111,112</sup> (a) by measuring the absorption of blue-green light by the lead dithizonate in solution; (b) by measuring the absorption of red light by the excess dithizone in the solution, and referring the results to a standard curve constructed under the same conditions; or (c) by measuring the transmittancy of the dithizone-lead dithizonate solutions at two wave lengths, 520 and 660 m $\mu$ , which correspond to regions of strong absorption by lead dithizonate and dithizone, respectively. The lead concentration is then determined from a nomograph in which the concentration is referred to the logarithms of the transmittancies of the two wave lengths.<sup>113</sup>

If lead is to be determined by measuring the absorption of red light, most of the original dithizone must remain in the organic solvent. This condition is attained by using a chloroform solution of dithizone and adjusting the pH of the

aqueous phase to 9.5-10. When the extraction is carried out in this way, most of the lead is present in the system as the dithizonate, and the partition of dithizone between the organic and aqueous phases is more sensitive to slight changes in pH than is the partition of lead dithizonate. Consequently, if there is any possibility of a slight variation in pH, the measurement of the absorption of blue-green light is to be preferred.

The color of the unknown lead solution may also be compared with the hues of a standard series similarly prepared, and containing known quantities of lead. The sensitivity is greatest at the ends of the series where the quantity of the metal is smallest and unchanged dithizone is greatest, and at the other end where the quantity of metal is largest and unchanged reagent smallest. Quantities of lead ranging from 0.0 to 200 $\gamma$  can be determined by this method with an error of within 5 per cent. A colorimetric titration technique may also be used.

These methods are illustrated by the following procedures, which are applied after isolating lead as described above.

(a) *Determination by absorption by lead dithizonate:* The following method is described by Sandell:<sup>204</sup>

**Reagents.** *Dithizone solution:* Dissolve 50 mg. of purified dithizone in 1 liter of redistilled chloroform. Store in the dark, and preferably in a refrigerator.

*Ammonia-cyanide solution:* Mix 20 g. of potassium cyanide and 150 ml. of concentrated ammonium hydroxide ( $d = 0.90$ ), and dilute to 1 liter with distilled water.

**Procedure.** Adjust the volume of the unknown solution, or a suitable aliquot of it, to 50 ml. with 1:100 nitric acid. Then add, according to the approximate amount of lead as determined during the isolation procedure (see above), a quantity of dithizone as indicated in Table 93. The dithizone solution required is prepared by diluting the standard reagent with pure chloroform, and the volume used is accurately measured.

TABLE 93.

Quantity of Lead $\gamma$	Concentration of Dithizone Solution mg. per Liter	Volume of Dithizone Solution ml.
0-5	5	5
0-10	10	5
0-25	10	10
0-50	10	20
0-100	10	35

To the resulting mixture, add 10.0 ml. of the ammonia-cyanide solution, and shake for 1 minute. Let stand until the liquids separate, and note the color of

the chloroform layer. If red, add an additional 5 ml. of 0.001 per cent dithizone solution, and again shake. Draw off the chloroform solution. Discard a small portion of the first liquid to run through the stem of the funnel. Transfer the remainder of the solution to a suitable absorption cell, and determine the extinction at 510  $\mu$ . Use water as the reference liquid. Prepare a standard curve for each lead range by using solutions containing known quantities of lead in 50 ml. of 1:100 nitric acid, saturating with chloroform, and treating in the same manner as the sample.

The following procedure, which is similar to the above, has been used by Clifford and Wichmann<sup>9</sup> for the determination of lead in urine.

**Reagents.** *Ammonia-cyanide solution:* Dissolve 75 ml. of concentrated ammonia and 10 g. of potassium cyanide in water and dilute to 500 ml.

*Citric acid solution:* Prepare a concentrated solution of citric acid and adjust to pH 3.5-4.0 with ammonium hydroxide. Then add a little copper salt and treat with hydrogen sulfide. Allow the mixture to stand and filter. Boil off the last trace of hydrogen sulfide and adjust the solution to a convenient concentration.

*Ash-aid solution:* Treat a concentrated solution of pure calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ ) with hydrogen sulfide, filter, and boil off the last trace of hydrogen sulfide. Recrystallize from water. Prepare a concentrated solution of aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and adjust the pH to 3.0-3.2 and treat with hydrogen sulfide. Dissolve 20 g. of the purified calcium salt and 40 g. of the aluminum salt in 100 ml. of redistilled water.

*Dithizone solution for extraction:* Dissolve 10-20 mg. of dithizone in 1 liter of redistilled chloroform.

*Standard lead solution:* The standard solutions are made up in 1 per cent nitric acid, and the volume of the standard lead solution and the pure 1 per cent nitric acid solution are so adjusted that in all cases the total volume is 50 ml. For example, in covering the range from 0 to 10  $\gamma$  of lead, it is convenient to use a solution of pure lead nitrate in 1 per cent nitric acid of such concentration that 1 ml. contains 1  $\gamma$  of lead. The 1  $\gamma$  standard is prepared by measuring 1 ml. of the standard solution and 49 ml. of pure 1 per cent nitric acid into a separatory funnel; the 5  $\gamma$  standard is prepared from 5 ml. of the lead nitrate solution and 45 ml. of the 1 per cent nitric acid; the 10  $\gamma$  standard from 10 ml. of the standard lead solution and 40 ml. of the nitric acid. The acid mixture is then made ammoniacal by adding 10 ml. of the ammonia-cyanide mixture. To eliminate differences in volume of extract between standard and unknown, both acid and standard lead solutions used in preparation of standards are saturated with chloroform before use.

*Standardized dithizone solution:* The color is developed by shaking out with a measured quantity of dithizone in chloroform. The volume and the strength of the standardized reagent solution depend upon the range of lead concentration to be covered. The volume of the reagent solution and its concentration are determined by reference to Table 94.

TABLE 94.

Lead Range $\gamma$	Volume ml.	Concentration of Dithizone Solution mg./liter
0-5	5	4
0-10	10	4
0-20	10	8
0-50	25	8
0-100	30	10
0-200	30	20

Filter the standards and determine the absorption coefficient ( $-\log$  transmittancy) in a cell of suitable size (see procedure below). From these data, construct a standardization curve.

**Procedure.** Measure 100 ml. of urine into a casserole and evaporate to dryness on a steam bath. Heat in a muffle at  $500^{\circ}$  C. and char for 15 minutes. Then add 2-3 ml. of the ash-aid solution dropwise so as to moisten all portions of the residue. Dry on a steam-bath and again heat in the muffle. If after 30 minutes the ash is not clean, remove, cool, reform the nitrates by adding 2 ml. of nitric acid, and dry and ash in the muffle. This should be repeated until the ash is clean.

When the ash is cooled, add 10 ml. of constant boiling hydrochloric acid and evaporate to dryness. Add a second 10-ml. portion of the constant boiling hydrochloric acid, and once more evaporate to dryness. Dissolve the residue in water and rinse into a separatory funnel with sufficient water to make the total volume 100 ml. Then add a quantity of the pure citric acid solution containing 5 g. of citric acid, and adjust the pH to 8.5 (thymol blue) with a measured volume of ammonia. Cool, add 5 ml. of 10 per cent potassium cyanide solution, and extract with two 20-ml. portions of dithizone in chloroform. Add the first 20 ml. in small portions with shaking between addition in order to obtain an approximate idea of quantity of lead present. Use more of the extracting solution if necessary. Combine the extracts and treat with two 25-ml. portions of 1 per cent nitric acid, using the second portion to wash out the funnel in which the nitric acid treatment is carried out. Filter the acid extracts through a small pledget of the moist, acid-washed cotton inserted in the stem of the funnel into a 50-ml. graduated flask or cylinder. Make up any slight deficit in volume with a few drops of 1 per cent nitric acid. Transfer the entire 50 ml. (or aliquot, if necessary, with the difference being made to 50 ml. with 1 per cent nitric acid) to another separatory funnel and add 10 ml. of the ammonia-cyanide solution. Shake well and add an appropriate volume of the standardized dithizone solution, depending upon the concentration of lead. Shake for 1 minute if the range is exceeded, as indicated by the color of the extract, re-extract with an excess of dithizone in chloroform, treat as before with 50 ml. of 1 per cent nitric acid and redevelop the color with standardized reagent covering a higher range. Allow the funnel to stand for a few minutes after color development, and

then filter off the chloroform solution through specially prepared filters. Folding a 9-cm. filter paper directly into the mouth of a 50-ml. low form beaker eliminates the use of a funnel. Transfer the liquid into a cell of proper dimension, and determine the absorption coefficient. Absorption coefficient as used here =  $-\log$  transmittancy. Suggested cell lengths for different lead concentrations are given in Table 95.

TABLE 95.

Lead Concentration $\gamma$	Length of Cell inches
0-5	2
0-10	2
0-20	1
0-50	1
0-100	$\frac{1}{2}$
0-200	$\frac{1}{2}$

Determine the lead content of the sample by reference to the standardization curve. A better method is to calculate the slope of the line connecting the standard points and also the intercept for zero lead on the absorption coefficient axis. Then the procedure for determining directly the lead content of an unknown falling within this range is to obtain the value of the absorption coefficient, subtract the intercept, and multiply by the standard lead factor.

(b) *Determination of absorption by excess dithizone*: The following method based on determining the absorption by the excess dithizone has been described by Guettel: <sup>208</sup>

**Reagents.** *Dithizone solution*: Use a solution containing 2, 4, or 12 mg. of purified dithizone per liter of redistilled chloroform.

*Ammonia-cyanide solution*: Mix 20 g. of potassium cyanide and 150 ml. of concentrated ammonium hydroxide ( $d = 0.90$ ), and dilute to 1 liter with distilled water.

**Procedure.** Dilute the lead solution, or an aliquot of it, to 50 ml. with 1:100 nitric acid and transfer to a 250-ml. separatory funnel. Add 10 ml. of the ammonia-cyanide solution, and then add 15 ml. of a solution of dithizone in chloroform. The concentration of the dithizone solution used depends on the quantity of lead present, and is determined by reference to Table 96.

TABLE 96.

Lead Concentration $\gamma$	Concentration of Dithizone Solution mg. per liter
0-5	2
0-15	4
15-50	12



Shake the mixture thoroughly, and allow the layers to separate. Filter, and immediately determine the transmittancy at 610 m $\mu$ . The lead content is obtained by reference to a calibration curve. Each calibration curve should be checked frequently, using in the procedure a standard lead solution equivalent to the lead concentration at the lowest portion of the useful range of the curve. For the curve corresponding to 0-15 $\gamma$  of lead, use 15 ml. of the dithizone solution containing 4 mg. of the reagent per liter of chloroform, and for the curve corresponding to 15-50 $\gamma$  of lead, use a 15 $\gamma$  lead standard. If the reading for these reference solutions deviates from the original calibration curves, displace all abscissas of the points on the curves in the same direction and for the same distance over the useful range of the curves, since in the latter region the curves are essentially parallel.

(c) *Standard series method*: The following procedure illustrates the standard series technique of colorimetric comparison in the lead determination of lead with dithizone.

**Reagents.** *Dithizone solution*: Dissolve 8-10 mg. of purified dithizone in 1 liter of redistilled chloroform.

*Ammonia-cyanide solution*: Mix 20 g. of potassium cyanide with 150 ml. of concentrated ammonium hydroxide ( $d = 0.90$ ), and dilute to 1 liter with distilled water.

Transfer an aliquot of the solution of lead in 1:100 nitric acid containing 0.5-3 $\gamma$  of the metal, to a 1.8 x 15 cm. glass-stoppered tube. Add 1.0 ml. of the ammonia-cyanide solution for each 5 ml of the lead solution, and 2.0 ml. of the dithizone solution. Shake vigorously for 10-15 seconds, allow the chloroform layer to settle, and then compare its hue with that of chloroform layers in a series of standards prepared in a similar manner from solutions containing known quantities of lead. View the colors against a white background.

Use 1.0 ml. of the dithizone solution if the unknown solution contains less than 0.5 $\gamma$  of lead.

(d) *Colorimetric titration*: Fischer and co-workers<sup>10</sup> have developed another system of mixed-color colorimetry by duplication rather than comparison with a standard series. The mixed-color is formed in the usual manner, and then the hue of the unknown is duplicated in a second vessel of the same shape and containing the same volume of dithizone and adjusted aqueous solution by alternately shaking and titrating into it a standard lead solution. When the hues are matched, the volume of the standard solution indicates the quantity of lead present. This method is said to be very accurate for quantities of lead ranging from 0 to 10 $\gamma$ .

**Reagents.** *Dithizone solution*: Dissolve 8-10 g. of purified dithizone in 1 liter of redistilled chloroform.

*Ammonia-cyanide solution*: Mix 20 g. of potassium cyanide with 150 ml. of concentrated ammonium hydroxide ( $d = 0.90$ ) and dilute to 1 liter with distilled water.

**Standard lead solution:** Use a freshly prepared 0.00100 per cent lead solution in 1:100 nitric acid. This is best prepared by diluting a 0.100 per cent solution just before use.

**Procedure.** Transfer the solution of lead in 1:100 nitric acid, or an aliquot of it containing up to 5 $\gamma$  of the metal, to a 1.8 x 15 cm. glass-stoppered tube. The volume of the solution used should not exceed 10 ml. Add 1.0 ml. of the ammonia-cyanide solution for each 5 ml. of the solution, and then with shaking after each addition, add a sufficient quantity of the dithizone solution to give a suitable mixed color for comparison. To a second similar tube add the same volume of 1:100 nitric acid, ammonia-cyanide solution, and dithizone reagent as contained in the first tube. Then from a buret graduated to 0.01 ml., add a 0.001 per cent lead solution to the comparison tube, with thorough shaking after each addition, until the hue of the chloroform layer matches that of the chloroform layer in the tube containing the unknown lead solution.

van Duuren<sup>114</sup> has used the Lovibond tintometer for the determination of lead and other metals by the dithizone method. A little dithizone is added to the solution of the lead salt, and, after standing, the solution is extracted with carbon tetrachloride. Extraction is repeated until the carbon tetrachloride is no longer colored. The color of the carbon tetrachloride solution of the dithizonate is then measured in a Lovibond tintometer against definite units of red, yellow and blue. This gives values from which, by reference to a diagram prepared from standard solutions, the lead content can be determined.

The mixed-color technique has been applied to the determination of lead in various materials. Basically the determination is carried out in essentially the manner described in the procedure above, although special treatment is required in most cases for preparing the sample or for the elimination of interference. Among the materials which may be determined in this manner are: urine, blood and various biological materials;<sup>74,77,115-117</sup> air;<sup>118-119</sup> pharmaceutical chemicals;<sup>112,120</sup> maple syrup;<sup>121</sup> water;<sup>122</sup> spray on fruits;<sup>53</sup> and foods.<sup>82</sup>

**The mono-color method.** In the mono-color method, lead is extracted with a small excess of dithizone in carbon tetrachloride, and the excess dithizone is removed from the combined extracts by washing with dilute ammonia, potassium cyanide or mixtures of the two. The quantity of lead extracted is then determined in two different ways: (a) The washed extract is shaken with dilute acid to convert the dithizonate into the equivalent quantity of green dithizone, which is measured by suitable means; or (b) the red color of the lead-dithizone complex may be measured directly as in the original mono-color method. Fischer and Leopoldi<sup>8,75</sup> measured the green color of the dithizone-carbon tetrachloride solution which was obtained by decomposing the extracted lead dithizonate with dilute acid. The excess dithizone used in extracting the lead was removed from the carbon tetrachloride solution with 5-ml. portions of 1:200 ammonia solution. These same authors<sup>78</sup> have used a similar method in which the excess reagent is removed with a 1 per cent potassium cyanide solution.

The following procedure illustrates the determination of lead by the mono-color method in which the green phase is measured:

**Reagents.** *Dithizone solution:* Dissolve 6 mg. of purified dithizone in 100 ml. of redistilled carbon tetrachloride.

*Ammonium citrate solution:* Dissolve 50 g. of ammonium citrate in 100 ml. of water. Make the solution ammoniacal (pH 8.5-9.0) and shake with successive small portions of dithizone solution until all lead has been removed. Remove any excess dithizone by shaking with carbon tetrachloride.

*Ammonium hydroxide:* Distill a concentrated solution of ammonia.

*Hydroxylamine hydrochloride solution:* Use a saturated solution of the analytical reagent in cold water. Prepare a short time before use. If necessary, purify as described in the procedure for the isolation of lead.

*Potassium cyanide solution:* Dissolve 50 g. of potassium cyanide in 100 ml. of water, and shake with successive small portions of dithizone solution until the final carbon tetrachloride extract is green in color. Remove dithizone from the aqueous layer by extracting with carbon tetrachloride, and dilute to 5 or 10 per cent.

**Procedure.** For determining 0.012-0.122 mg. of lead, best results are obtained if the original unknown solution contains approximately 0.5% of lead per ml. If metals precipitated by ammonia are present, add sufficient ammonium citrate to prevent their precipitation, and then make alkaline to litmus with ammonium hydroxide. Add sufficient 5 or 10 per cent potassium cyanide solution to convert foreign heavy metals into their cyanide complexes. This usually requires 3-5 ml. of 5 per cent potassium cyanide per 10 ml. of sample, but in the presence of much copper, silver and zinc, as much as 10 ml. of 10 per cent potassium cyanide may be needed. Add 1 ml. of the hydroxylamine hydrochloride solution, heat to boiling, and cool to room temperature.

Then shake the unknown solution with 3-5 ml. of the green dithizone solution in a separatory funnel. Withdraw the carbon tetrachloride solution and treat the aqueous phase with a second portion of the dithizone reagent. This should be repeated until the red color due to lead dithizonate is no longer observed in the carbon tetrachloride solution. To the combined extracts containing the lead dithizonate, add 5 ml. of 0.075 N ammonium hydroxide to remove the excess dithizone. Shake and separate the aqueous layer. Again shake with a second 5-ml. portion of ammonia and separate. By this treatment only the lead compound remains in the carbon tetrachloride layer. Dilute the latter to a definite volume with pure carbon tetrachloride, and shake with dilute hydrochloric or sulfuric acid to revert the red dithizonate to green dithizone. Compare the resulting green color with standard solutions similarly prepared and containing known quantities of lead.

The final determination of lead can be carried out in several different ways. After diluting the lead dithizonate solution to a definite volume with carbon tetrachloride, the transmittancy may be determined with a spectrophotometer or a filter photometer. A filter giving maximum transmission at 520-530  $m\mu$  is satisfactory. The lead concentration is determined by reference to a calibration

curve. Comparison may be made with a standard lead dithizonate solution with the aid of a Duboscq colorimeter, or by the standard series method.

A 0.5 per cent, lead-free solution of potassium cyanide may be used to remove the excess dithizone instead of ammonia.

For quantities of lead ranging from 0.01 to 0.12 mg., the error by this method ranges from 0.001 to 0.003 mg., or 3-8 per cent.

By using the above procedure, 0.05 per cent of lead can be determined with accuracy in samples of so-called "pure" zinc, cadmium, copper, copper sulfate, mercury, silver, arsenic, tin, aluminum, and beryllium. Stannous and thalious salts interfere and must be oxidized to the stannic and thallic state before applying the procedure described above. Bismuth interferes and must be removed.

**Determination of lead in the presence of much bismuth.** Although the mono-color method is less accurate than the mixed-color method, the former is more readily adaptable to the determination of lead in the presence of much bismuth and thallium.

Lead may be determined in the presence of more than 1 mg. of bismuth by the following procedure:<sup>204</sup>

**Reagents. Dithizone solution:** Dissolve 3 mg. of dithizone in 100 ml. of carbon tetrachloride.

**Ammonium citrate solution:** Dissolve 50 g. of ammonium citrate in 100 ml. of water. Adjust the pH to 8.5-9 with ammonia, and shake with successive portions of a dithizone solution containing 50 mg. of the reagent per liter of carbon tetrachloride until all lead is removed. Remove any excess dithizone by shaking the aqueous layer with carbon tetrachloride.

**Potassium cyanide solution:** Dissolve 10 g. of lead-free potassium cyanide in 100 ml. of water. If necessary, remove lead by extracting with a carbon tetrachloride solution of dithizone.

**Procedure.** The sample solution should not contain more than 25% of lead nor more than 5 mg. of bismuth. Add 1 ml. of ammonium citrate solution, and then make alkaline to litmus with ammonia. For each 10 ml. of solution, add 10 ml. of 10 per cent potassium cyanide solution, and shake thoroughly with 2 ml. of dithizone solution. Separate the carbon tetrachloride solution, and repeat the extraction with a second 2-ml. portion of the dithizone reagent.

Continue the extractions until the last 2-ml. portion has the pure orange color of bismuth dithizonate. To test for completeness of the lead extraction, shake the last portion of the carbon tetrachloride extract with 3 small portions of 1 per cent potassium cyanide solution. No pink color should appear in the carbon tetrachloride layer. A pink color indicates the necessity of an additional extraction with dithizone.

Combine all the extracts, which contain all the lead and some bismuth, and shake with 5 ml. of 1:100 nitric acid. Separate the aqueous phase, and adjust the pH to 2.8-3. This is indicated by the full yellow color of thymol blue. Shake with small portions of dithizone solution (containing 6 mg. of dithizone per 100 ml. of carbon tetrachloride) until the dithizone solution remains pure green.

Remove the excess dithizone from the aqueous solution with carbon tetrachloride, and carry out the lead determination as described in the above procedure, after making alkaline with ammonia, adding 5 ml. of 5 per cent potassium cyanide, and 1 ml. of hydroxylamine hydrochloride.

**Determination of lead in the presence of thallium.** The mono-color method is applied as follows to the determination of lead in the presence of thallium:

**Reagents.** For a description of reagents used, see page 500.

**Procedure.** To the lead solution, which may contain as much as 500 $\gamma$  of thallium, add 0.5-1.0 ml. of ammonium citrate solution, and add ammonium hydroxide until slightly alkaline. Add 10 ml. of 10 per cent potassium cyanide, and extract with 2-ml. portions of a dithizone solution containing 4 mg. of dithizone per 100 ml. of carbon tetrachloride. Continue the extractions until all lead is removed. Since some thallium is extracted, and since both thallium and lead dithizonates are red in color, completeness of the lead extraction cannot be distinguished by a color change. The following test, however, is applied: Shake each extract with twice its volume of 0.5 per cent potassium cyanide. The carbon tetrachloride solution is decolorized if the color is due to thallium alone, but not if lead dithizonate is present.

Combine the carbon tetrachloride extracts, and shake with 0.5 per cent potassium cyanide solution to remove any excess dithizone. Dilute to a definite volume with carbon tetrachloride, and determine lead by the mono-color method.

Results obtained in the determination of lead in the presence of bismuth and thallium are shown in Table 97, which is taken from data compiled by Fischer and Leopoldi.<sup>75</sup>

TABLE 97.—DETERMINATION OF LEAD WITH DITHIZONE IN THE PRESENCE OF BISMUTH AND THALLIUM

Bismuth mg.	Thallium mg.	Lead Used $\gamma$	Lead Found $\gamma$	Error $\gamma$
0.1 <sup>a</sup>	....	9.5	10.0	+0.5
0.1 <sup>a</sup>	....	9.5	9.0	-0.5
0.5 <sup>a</sup>	....	18.7	17.7	-1.0
1.0 <sup>a</sup>	....	7.4	7.1	-0.3
1.0 <sup>a</sup>	....	7.4	8.3	+0.9
5.0 <sup>b</sup>	....	9.8	8.3	-1.5
5.0 <sup>b</sup>	....	7.4	6.9	-0.5
....	0.15	9.5	10.6	+1.1
....	0.3	4.8	4.2	-0.6
....	0.75	9.5	8.2-10.6	-1.3 to +1.1

<sup>a</sup> Bismuth extracted with dithizone at pH 2.8-3.0.

<sup>b</sup> Fractional extraction of lead from cyanide medium, followed by removal of coextracted bismuth at pH 2.8-3.0.

Evlanov<sup>88</sup> states that the method of Fischer and Leopoldi<sup>73</sup> can be used in the presence of alkali and alkaline earth metals, which do not give complexes with dithizone. Many of the heavy metals such as zinc, nickel, iron, copper, mercury, bismuth, tin and silver are converted into non-interfering cyanide complexes prior to treatment with dithizone. Since 10-200 $\gamma$  of lead can be determined by this method, it may be used for the determination of lead in food products. Similar procedures have been employed for the estimation of lead in special materials, such as milk,<sup>89</sup> urine,<sup>90</sup> oil,<sup>20</sup> zinc and zinc alloys<sup>91</sup> and biological materials.<sup>92,93</sup>

Seelkopf and Taeger<sup>84</sup> and others<sup>72,94</sup> have used the method of Fischer and Leopoldi<sup>8,73</sup> for the removal of excess dithizone, but instead of reverting the lead dithizonate to the free reagent they determined the extinction coefficient of the red phase with a Zeiss-Pufrich photometer and a green filter (530  $m\mu$ ). Their error in determining 0.005-0.02 mg. of lead ranges from 1-10 per cent.

Winter and co-workers<sup>51</sup> used chloroform instead of carbon tetrachloride as the solvent for dithizone, and removed the excess dithizone with a more alkaline solution. The red color of the lead dithizonate was matched in an ordinary colorimeter with that of a standard solution set at ordinary depth. The following procedure, taken from the work of Winter and co-workers,<sup>51</sup> is typical of the one-color method in which the red phase is measured.

**Reagents.** *Dithizone solution:* Dissolve 10 mg. of dithizone in 400 ml. of chloroform.

*Cyanide-citrate solution:* Add 30 ml. of 5 per cent potassium cyanide solution to 450 ml. of water, and then add 15 ml. of a 5 per cent aqueous solution of ammonium citrate that has been made slightly alkaline with ammonium hydroxide, and finally add 5 ml. of ammonium hydroxide.

This reagent should be tested for the absence of lead as follows: Place 20 ml. of the solution in a small separatory funnel, add 1 ml. of the dithizone solution and 5 ml. of chloroform. Shake, separate, and extract the chloroform solution once or twice with another 20 ml. of the cyanide-citrate solution. The final chloroform layer should be colorless or only faintly red. If a red color indicates the presence of lead, treat as follows: Add a few ml. of dithizone solution and 15 ml. of chloroform and shake vigorously for 5 minutes. Allow 5 minutes for the layers to separate. If the chloroform layer is red and the aqueous layer colorless, repeat the process. Draw off the chloroform, and again extract by adding 1 ml. of dithizone and 10 ml. of chloroform each time until the chloroform layer is practically colorless or slightly green.

*Alkaline potassium cyanide solution:* Add 10 ml. of 5 per cent potassium cyanide solution and 5 ml. of ammonium hydroxide to 500 ml. of water.

This solution should also be lead-free. Lead is removed by employing the same procedure as described under the cyanide-citrate solution.

*Standard lead solution:* Dissolve 1.5985 g. of recrystallized lead nitrate in 100 ml. of 0.1 per cent nitric acid and dilute 0.5 ml. of this solution to 500 ml. One ml. of this solution contains 0.01 mg. of lead.

**Preparation of sample.** If the material is a solid, place from 1-5 g. of the material, depending upon the quantity of lead present, in a porcelain crucible and add 1 ml. of 1:10 sulfuric acid. Add sufficient distilled water to moisten the sample thoroughly and mix. Dry at 100° C., and then burn in a muffle at 500° C. If the sample is a liquid, add the sulfuric acid, evaporate to dryness, and then proceed as with the solid.

Moisten the ash in the crucible, add 1 ml. of concentrated hydrochloric acid, and heat the crucible on a steam-bath for several minutes. Then add 2 ml. of 1:5 nitric acid, transfer to a small beaker, and make just alkaline to litmus with ammonia hydroxide. Add 2 ml. of 5 per cent citric acid, and again make alkaline with ammonium hydroxide. If a precipitate forms which does not redissolve on heating, add hydrochloric acid until the solution is clear, and then add 2 ml. in excess. Silicates may be present, and these do not dissolve. Finally make the mixture just alkaline with ammonium hydroxide.

**Determination of lead.** Transfer a quantity of the solution containing about 0.01 g. of lead to a 150-ml. separatory funnel and add 15 ml. of the cyanide-citrate solution and an excess of dithizone solution. The latter should be added in 1-ml. portions from a buret, and with vigorous shaking after each addition. An excess of dithizone is indicated by the appearance of a purple color in the chloroform layer. Now add chloroform from a buret to make the total volume exactly 10 ml. Transfer the chloroform layer to a second separatory funnel containing 20 ml. of the alkaline potassium cyanide solution. Shake the mixture to extract the excess dithizone, allow the layers to separate, and then remove the aqueous layer. Repeat the extract with 20-ml. portions of alkaline potassium cyanide solution until the complete removal of dithizone is indicated by a colorless aqueous extract. During the last separation, open the stopcock of the separatory funnel slightly until chloroform replaces the water in the bore. Remove the moisture from the stem of the funnel with a cotton swab, and draw off the clear or slightly turbid chloroform layer into a dry test tube, retaining in the separatory funnel any small quantity of emulsion which may have formed at the interface of the liquids during the separation. Allow the solution to stand in the test tube for 3-4 hours until the solution is clear, and then compare the cherry red color of the lead dithizonate in a colorimeter with standard solutions similarly and simultaneously prepared.

Since the intensity of the color is not proportional to the lead content, it is necessary to construct a curve representing the colorimeter readings of standard solutions containing known quantities of lead. This is accomplished as follows: Make determinations on four series of standard lead solutions, each consisting of 10 samples containing 0.0010, 0.0025, 0.0050, 0.0100, 0.0150, 0.0200, 0.0250, 0.0300, 0.0350, and 0.0400 mg. of lead respectively. Each is read against 0.02 mg. of lead as a standard. The colorimeter readings are made with the standard set at 20, or when this is not practical, they should be calculated to this value. The relation between the quantity of lead and colorimeter readings is illustrated in Table 98, which is taken from the work of Winter and co-workers:<sup>51</sup>

TABLE 98.

Lead Present mg.	Average Readings
0.0010	160.0
0.0025	119.0
0.0050	68.8
0.0100	38.2
0.0150	26.1
0.0200	20.0
0.0250	16.7
0.0300	14.7
0.0350	13.1
0.0400	12.1

The results obtained in a series of measurements by the above procedure are shown in Table 99.

TABLE 99.—DETERMINATION OF LEAD BY THE MONO-COLOR METHOD

Colorimeter Reading	Lead Present mg.	Lead Found mg.	Error	
			mg.	Per Cent
54.5	0.0070	.0067	—0.0003	—4.3
44.0	0.0080	.0084	+0.0004	+5.0
32.8	0.0120	.0120	0.0000	0.0
32.5	0.0125	.0120	—0.0005	—4.0
32.6	0.0125	.0121	—0.0004	—3.2
29.0	0.0135	.0134	—0.0001	—0.7
23.8	0.0165	.0167	+0.0002	+1.2
23.7	0.0175	.0169	+0.0006	—3.5
23.7	0.0175	.0169	+0.0006	—3.5
17.8	0.0225	.0228	+0.0003	+1.3
16.8	0.0250	.0250	0.0000	0.0

Interference by other metals with this determination has been discussed in previous sections.

Ross and Lucas<sup>96,97</sup> use about the same procedure for the determination of lead in urine. Tompsett and Anderson<sup>72,98,99</sup> have used a similar procedure for determining lead in water and biological materials after a preliminary separation with diethyldithiocarbamate. The method has also been used for the determination of lead in urine, blood and feces,<sup>100-102</sup> in organs, bones and serous fluids<sup>109</sup> and in air.<sup>110</sup>

This method, like that in which the green color of the reverted dithizone is measured, is subject to some error, due to the incomplete removal of the excess reagent, and the slight solubility of lead dithizonate in an alkaline wash solution. Jewlanowa<sup>207</sup> has determined lead in very dilute solutions by comparing



the color formed in the dithizone reaction with colored glass slides in a comparator. The excess dithizone is removed with a dilute potassium cyanide solution.

**Determination of lead by extractive titration.** In extractive titration procedures, lead is extracted from the aqueous solution of definite pH with successive increments of standardized dithizone solution until the green color of the reagent is no longer changed to red. The end-point of the titration is indicated by the failure of the green solution to turn red, due to the formation of the dithizonate. The titration is carried out in a separatory funnel with sufficient shaking between additions to establish equilibrium between the lead and dithizone, and the solvent layer containing the red lead complex is drawn off from time to time. The dithizone solution is standardized against a lead solution of known concentration in the same manner. This principle has been applied by Bonnenkamp and Linneweh<sup>67</sup> and others<sup>50,123,124</sup> to the determination of lead in urine; by Fischer<sup>17</sup> to the determination of silver, zinc and cadmium; and by Winkler<sup>24</sup> to the determination of mercury.

Wilkins and co-workers<sup>49,71</sup> have developed a satisfactory method using this principle for the determination of lead in biological materials. The lead is isolated with dithizone from the biological material, and is then transferred to the aqueous phase by shaking the chloroform solution of the dithizonate with 1 per cent nitric acid. The pH is then adjusted to 7.5 and the solution titrated with standardized dithizone solution according to the accepted technique. This method is claimed accurate and sensitive to 0.001 mg. of lead.

The following procedure may be used for the determination of lead in blood:

**Reagents. Citric acid solution:** Dissolve 40 g. of citric acid monohydrate and 1 g. of salicylic acid (preservative), in sufficient water to make 1 liter of solution.

**Sodium chloride-hydrochloric acid solution:** Saturate a 5 per cent hydrochloric acid solution with sodium chloride at room temperature.

**Dithizone extraction solution:** Dissolve 40 mg. of dithizone in a liter of chloroform.

**Dithizone titration solution:** The reagent used for the titration must be purified as follows: Dissolve 0.1 g. of commercial dithizone in 30 ml. of chloroform in a large separatory funnel and extract the resulting solution once with 900 ml. of 0.5 per cent ammonium hydroxide solution. Draw off the chloroform solution and neutralize the aqueous phase with 10 per cent hydrochloric acid to litmus. Extract the purified dithizone thus precipitated with chloroform. The chloroform solution is then diluted so as to be equivalent to 0.01 mg. of lead per ml. (the total volume should be about 1400 ml. depending upon the purity of the original material).

The dithizone titration solution is standardized as follows: Transfer 5 to 20 ml. of a standard lead solution of recrystallized lead nitrate (containing 0.01 mg. of lead per ml.) to a 125-ml. separatory funnel. If less than 20 ml. is used, make

the total volume 20 ml. by adding water. Add 2 ml. of 10 per cent potassium cyanide solution and 2-3 drops of phenol red, and then adjust the pH to 7.5 with 5 per cent nitric acid. If 0.20 mg. of lead is used for the standardization, deliver 10 ml. of the dithizone solution from a buret to the separatory funnel and then shake the mixture vigorously. Continue the shaking until no further increase in the depth of the orange-red color is produced. Allow the layers to separate and draw off and discard the chloroform layer. Then add 5 ml. of the dithizone solution to the separatory funnel and repeat the extraction. About 0.1 ml. of the chloroform phase should be left in the separatory funnel after each extraction to prevent loss of the aqueous solution. Continue the extraction, using smaller and smaller quantities of the dithizone solution and removing each chloroform extract before the next portion is added. Near the end of the titration, the dithizone reagent is added in 0.1-ml. and finally in 0.05-ml. portions. A few drops of chloroform is added to give sufficient volume for observing the color produced. There comes a time when the green color of the added reagent changes to a purple shade that persists after prolonged and vigorous shaking. The next 0.05 ml. portion of dithizone should remain practically unchanged in color. The end-point is reached when the green color of the reagent remains unchanged. Read the total volume of dithizone solution from the buret. Make a blank determination in exactly the same manner by using 20 ml. of water in place of the lead nitrate solution. The lead equivalents of the reagent are calculated after subtracting the blank correction. The solution must be standardized each day because of deterioration of the reagent.

**Preparation of the sample.** Destroy the organic matter in 10-15 g. of whole blood by wet oxidation in a Kjeldahl flask as follows: add 15 ml. of concentrated nitric acid and concentrate the digest to a little less than 5 ml. Add 2 ml. of concentrated sulfuric acid and heat until the oxides of nitrogen are completely expelled. Then increase the temperature until fumes of sulfur trioxide are evolved, and add dropwise 2 ml. of perchloric acid. Continue fuming of sulfur trioxide for about 5 minutes. The final volume is about 3 ml.

Cool, add 5 ml. of water, and dissolve the residue by adding 5 ml. of the sodium chloride-hydrochloric acid solution and heating. Make just alkaline to litmus with ammonium hydroxide and add 5 ml. of 4 per cent citric acid solution to dissolve the precipitated ferric hydroxide. Next add 2 ml. of 10 per cent potassium cyanide solution, and make the mixture just alkaline to litmus with ammonium hydroxide. Add 1-2 additional drops of ammonium hydroxide and transfer the solution to a 250-ml. separatory funnel. Rinse the flask thoroughly with water.

**Separation of lead.** To insure the complete removal of lead from the Kjeldahl flask, add a drop of 10 per cent potassium cyanide solution, 0.5 ml. of water and 5 ml. of the dithizone extraction solution. Shake vigorously and transfer, with thorough rinsing, to the 250-ml. separatory funnel containing the sample and shake well. Separate the chloroform extract and repeat the extraction with successive 5-ml. portions of the dithizone solution until the color of a new portion of dithizone undergoes no change in color. Then extract the aqueous solution once more to insure the complete removal of lead. Collect

the chloroform extracts in a 125-ml. funnel. Note the volume of dithizone solution used, since from this a preliminary indication of lead present is obtained.

Wash the chloroform extract with 25 ml. of water containing 1 drop of 10 per cent potassium cyanide solution, and separate quantitatively. Transfer the chloroform extract to another 125-ml. separatory funnel, and remove the lead from the dithizonate by shaking the chloroform solution with 10 ml. of 1 per cent nitric acid. Separate completely the aqueous phase, which contains the lead as lead nitrate, and wash once with pure chloroform. Combine the chloroform solution and the wash solution and re-extract with a second 10-ml. portion of 1 per cent nitric acid. Separate and wash this aqueous solution as before, and combine with the first lead nitrate solution. Wash the combined aqueous solutions repeatedly with small portions of chloroform until a freshly added portion remains colorless.

Prepare the lead nitrate solution for the extractive titration as follows: If the solution contains more than 0.2 mg. of lead, dilute to a known volume and use an aliquot for the final analysis. Add to the lead nitrate solution, or a suitable aliquot containing about 0.2 mg. of lead, 2 ml. of 10 per cent potassium cyanide solution and 2-3 drops of phenol red, and then add 5 per cent ammonium hydroxide dropwise until the pH is adjusted to 7.5.

**Determination of lead by extractive titration.** Finally, determine lead by titrating with the dithizone titration solution in exactly the same manner as used for standardizing the reagent. From 15 to 25 per cent of the total volume estimated as necessary is used in the first extraction. The extractions are then continued using smaller and smaller quantities of dithizone as previously described. Blanks are prepared by using the same quantities of all the reagents as are required in the analysis, and are determined simultaneously with the sample and in identical apparatus.

In the event the end-point is overrun, re-extract the lead and repeat the titration.

Results obtained using this method when applied directly to pure solutions of lead nitrate and lead chloride are given in Table 100.

Reith and van Dijk<sup>70</sup> have used a somewhat similar procedure for the determination of lead in the presence of thallium and bismuth. Horwitt and Cowgill<sup>50</sup> have proposed a variation of the extractive titration procedure. They extract lead with an excess of dithizone, remove the excess reagent with a very weak cyanide solution, revert the lead dithizonate to the equivalent quantity of dithizone and then titrate this with a standard lead solution.

The extractive titration procedure is sound in principle, but the methods are generally slow and tedious and the end-point is easily overrun. The titration should be conducted at a pH of relative stability of the lead dithizonate; hence, the method of Wilkins and co-workers<sup>49,71</sup> appears to be somewhat inadequate. It appears that considerably more than the equivalent quantity of dithizone is required to attain the end-point of pH 7.5, and at higher pH the end-point (color change from red to green) is much more abrupt and less shaking is required. If the pH is too high, an emulsion may be formed, and at pH 11 or

TABLE 100.—DETERMINATION OF LEAD BY EXTRACTIVE TITRATION IN THE ABSENCE OF OTHER METALS

Lead Used mg.	Lead Found mg.	Error mg.
as $\text{PbCl}_2$		
0.500	0.500	0.000
0.500	0.500	0.000
0.200	0.199	-0.001
0.100	0.100	0.000
0.100	0.101	+0.001
0.100	0.100	0.000
as $\text{Pb}(\text{NO}_3)_2$		
0.100	0.100	0.000
0.050	0.051	+0.001
0.050	0.049	-0.001
0.050	0.051	+0.001
0.010	0.010	0.000

above the lead dithizonate in the absence of excess dithizone is appreciably soluble in the aqueous phase. Clifford and Wichmann<sup>9</sup> recommend a pH of 9.5 as most satisfactory. This is indicated by the appearance of an incipient blue color with thymolphthalein.

**Determination of lead dithizonate by titration with bromine.** Dithizone is readily oxidized by bromine, and this property has been used by Hibbard<sup>46,47</sup> for the determination of zinc after the extraction with dithizone. The separated zinc dithizonate is oxidized with an excess of standard bromine in carbon tetrachloride, and the excess bromine is then determined with potassium iodide and sodium thiosulfate. According to Hibbard<sup>19</sup> lead can be determined in a similar manner. For the details of this method, see section on determination of zinc (page 534).

Because of many interferences with the dithizone method for lead, special procedures are often required for determining lead in different materials. A number of such materials and references pertaining to their analysis are listed in Table 101.

**Detection and determination of mercury.** **Detection of mercury.** When mercury salts are shaken with a green solution of dithizone in carbon tetrachloride, the carbon tetrachloride layer is colored orange by the formation of mercury dithizonate. This reaction has been used by various investigators as a sensitive test for mercury.<sup>5,125-129,191</sup> The test may be carried out as a drop reaction as follows:

**Procedure.** Mix a drop of the solution to be tested with 2 drops of a reagent prepared by dissolving 6-20 mg. of dithizone in a liter of carbon tetrachloride. Allow the mixture to evaporate and dissolve the residue in a little carbon tetrachloride. The green color of dithizone is changed to orange if

TABLE 101.—DETERMINATION OF LEAD IN VARIOUS MATERIALS  
WITH THE AID OF DITHIZONE

Material	Reference Number
Biological materials (general) .....	54, 55, 92, 93, 103, 117, 208
Blood .....	9, 49, 50, 71, 100, 101, 102
Urine .....	9, 50, 67, 71, 72, 74, 90, 96, 97, 99, 100, 115
Bones .....	33, 50, 109
Tissue .....	71, 72, 99, 109
Serous fluids .....	109
Feces .....	100
Toxicological examination of organic matter .....	22, 67, 78, 86, 87, 94, 104, 105, 123, 124, 193, 196
Food products .....	18, 32, 51, 52, 53, 69, 70, 82, 88, 106, 107, 186
Milk .....	9, 89
Water .....	83, 98, 122
Maple syrup .....	121
Air .....	108, 110, 118, 119
Cosmetics and pharmaceuticals .....	112, 120, 189
Dyes .....	28, 29, 30, 31
Calcium phosphate .....	34, 35
Zinc and zinc alloys .....	91
Oil .....	20
Plants .....	186
Foods .....	186
Medicinals .....	187
Corrosion resistant steel .....	195
Steel .....	200
Brass .....	200
Magnesium base alloys .....	202

mercury is present. As little as 0.25 $\gamma$  of mercury (as mercuric chloride) can be detected at a concentration of 1:200,000.

Since many other metals also form complexes with dithizone, various modifications of the above procedure are necessary to eliminate interference when other cations are present. This may be accomplished by complex formation, proper adjustment of the pH of the solution and by the oxidation of complex forming ions. In acid solution the only interfering metals are tin, antimony, bismuth, copper, gold and the platinum metals.

Interference by tin and iron is eliminated by oxidation, while antimony and bismuth complex salts with tartaric acid do not give a color reaction with dithizone. If bismuth is present, nitric acid should be added. Interference by gold is eliminated by reducing with sulfurous acid solutions, and the platinum metals are similarly eliminated by the addition of copper or silver powder. If copper is present, the solution to be tested is neutralized and then made appreciably acid with 95 per cent formic acid before treating with the reagent solution. Under these circumstances the carbon tetrachloride layer is pink in color and then turns bright yellowish-orange in the presence of mercury.

If copper, iron, cobalt, nickel, platinum, and gold are present, the solution to be tested is first treated with copper powder to precipitate gold, platinum and mercury. Only copper and mercury are dissolved by treating the precipitate

with nitric acid, and the mercury can be detected in the presence of copper as described above. If copper is absent, the platinum metals are precipitated with silver powder, and mercury is then detected in the filtrate. Silver does not interfere, since the silver does not react with dithizone even in low acid concentration. As little as 1 $\gamma$  of mercury can be detected in the presence of 100,000 $\gamma$  of silver by adding 1 drop of 1 N sulfuric acid to the solution to be tested before treating with dithizone.<sup>125</sup> Fischer<sup>130</sup> has stated that oxidizing agents disturb the mercury reaction.

A 2 per cent solution of dithizone in pyridine has been used by Llacer<sup>201</sup> for the microchemical detection of mercury. The test is applied in a dilute nitric acid solution of pH 0.5-1.0, and mercury is recognized by the characteristic microcrystals which form.

**Determination of mercury.** Mercuric mercury reacts with an excess of dithizone in a solution which is 1 N in mineral acid to form an orange-colored keto complex which is soluble in chloroform and carbon tetrachloride. Mercurous mercury gives a yellow color under the same conditions. This reaction can be used for the colorimetric determination of mercury.<sup>131</sup> The mixed color technique is the most suitable for this purpose. Either a carbon tetrachloride or chloroform solution of dithizone may be used. The yellow color of mercury dithizonate persists as long as mercury is present in excess, but an excess of dithizone causes the solution to turn red or reddish violet, depending upon whether traces of copper are present.

Other metals reacting with dithizone in an acid solution are copper, gold, palladium, bivalent platinum and silver.

Copper in excessive concentrations must be removed, and this is accomplished by the addition of potassium iodide. In the presence of potassium iodide copper can be extracted with dithizone, while the mercury remains in solution. Mercury cannot be extracted or titrated with dithizone in an acid solution when iodides are present, but it can be extracted from an ammoniacal solution. It can also be extracted from acid solutions by a solution of sodium diethyldithiocarbamate in chloroform.<sup>24</sup>

According to Fischer<sup>17</sup> and Wolbling and Steiger,<sup>128</sup> bismuth, stannous tin, antimony, gold, and the platinum metals interfere with the determination of mercury with dithizone. In acid solutions, however, only bismuth, tin, antimony, gold, copper and platinum interfere. Interference by stannous tin may be eliminated by oxidation. Chlorides are used to prevent interference by silver in an acid solution, and tartaric acid prevents interference by antimony and bismuth, also in acid solution. Interference by bismuth, tin or cadmium is prevented by using a solution containing 1 per cent nitric acid. Gold and platinum are precipitated with powdered copper. Mercury is also precipitated by this treatment, but it may be redissolved with nitric acid while the gold and platinum remain insoluble. The determination of mercury by the dithizone method is not prevented by the presence of chlorides.

Mercury can be recovered from acid solutions as strong as 6 N and from sodium hydroxide solutions up to 2 N.

Winkler<sup>25</sup> has used a modification of the Fischer procedure for the separation and determination of mercury in organic materials.

**Reagents. Dithizone solution:** A 0.05 per cent solution of dithizone in carbon tetrachloride. One mg. of mercury combines with 2.6 mg. of dithizone. This solution does not keep more than 1 month.

**Dithizone extraction solution:** Transfer 20 ml. of the above solution to a 200-ml. volumetric flask, and dilute to the mark with chloroform.

**Dithizone titrating solution:** Transfer 2.5 ml. of the dithizone solution to a 100-ml. volumetric flask and dilute to volume with carbon tetrachloride.

**Tartaric acid solution:** Extract a 10 per cent aqueous solution of tartaric acid with dithizone to remove all mercury.

**Standard mercury solution:** Dissolve 0.1 g. of mercury in a little nitric acid and dilute to 1 liter. One ml. of this solution contains 0.01 mg. of mercury.

**Preparation of the sample:** If mercury is to be determined in organic matter, weigh a quantity of the material containing about 0.03 mg. of mercury and digest with nitric acid. Then add a 5 per cent potassium permanganate solution until the purple color persists when the liquid is heated to 70° C. Cool and add a little hydrogen peroxide dropwise to dissolve the precipitated manganese dioxide. Nitric acid must be present. Remove any sodium nitrite that may be formed by adding 0.5-1.0 of hydroxylamine sulfate.

**Extraction of mercury:** If antimony is present, add 15 ml. of 10 per cent tartaric acid previously extracted several times with dithizone solution to remove mercury. The solution should have a concentration of at least 1 per cent free nitric acid. To concentrate the mercury and remove interfering substances, extract the solution in portions not to exceed 425 ml. as follows: To the solution contained in a 500-ml. separatory funnel, add 20 ml. of the dithizone extraction solution and shake for 20 seconds. If the chloroform layer is not yellow in color, indicating an excess of dithizone, draw off the extract and repeat the extraction with a 15-ml. portion of the dithizone extraction solution. If still yellow, again draw off and extract with a 20-ml. portion of the reagent. Continue the extraction until a green or reddish color is obtained; then extract once more using 15-ml. of the reagent.

**Determination of mercury:** The mercury may now be determined by a method of extractive titration or by the comparative method of Fischer.<sup>181</sup> For the determination by extractive titration proceed as follows:

If copper is absent, or present only in very small quantities, add to the combined extracts in a separatory funnel 50 ml. of water and 10 ml. of a 5 per cent solution of potassium permanganate. Acidify with 1 ml. of 1:1 sulfuric acid and shake vigorously for 1 minute. Then add 30 per cent hydrogen peroxide dropwise until the solution is clear, shaking gently after each addition of a few drops. When the solution is clear, shake for 1 minute and allow the liquids to separate. Discard the chloroform layer, and to the aqueous solution add hydro-

chloric acid if silver is present, or suspected of being present. If only very small quantities of mercury are present, use the entire solution for the determination, but when 0.1-3 mg. of mercury is present, dilute to a suitable volume and use an aliquot for the determination.

If copper is present in large quantities proceed as follows: Shake the combined dithizone extracts with 60 ml. of an aqueous solution containing a few drops of 1:1 sulfuric acid, a few crystals of potassium iodide and a few drops of 5 per cent sodium arsenite solution. Shake vigorously for 20 seconds and then carefully separate the chloroform solution. Wash the aqueous solution with a little chloroform. By this treatment mercury is transferred to the aqueous phase and the copper is removed.

For the titration, fill two burets with the dithizone titrating solution and place 10 ml. of the standard mercury solution in a second separatory funnel. Dilute to about 100 ml. with water, and add a few drops of 1:1 sulfuric acid. Now make a preliminary titration and save the extracts by carefully withdrawing into another separatory funnel. Make preliminary titration as follows: Add to the unknown solution from buret number one, 4 ml. of the dithizone solution and close the funnel. Shake a few times, then invert and open the stopcock to relieve the pressure. Close the funnel, shake vigorously for 10 seconds and allow the liquids to separate. To the standard solution in the other funnel, add 1 ml. of the reagent solution from buret number two. Shake and allow the liquids to separate. Now compare the color of the chloroform layers in both funnels and continue adding the dithizone solution in 4-ml. portions to the unknown, shaking as above after each addition. After each second addition, draw off the carbon tetrachloride layer into the second separatory funnel until on separation the yellow color due to the mercury compound is replaced by another color, usually green. About 20 ml. of the reagents are required.

Reoxidize the combined extracts with potassium permanganate, and remove the excess oxidizing agent as directed in the above procedure. Titrate a second time by adding to the aqueous solution thus obtained 5-6 ml. less of the titrating solution than was added before the end-point was reached in the preliminary titration. Shake and draw off the extract, and complete the titration with 1-ml., and finally with 0.5-ml. portions, drawing off the extract after each second addition.

One ml. of the titrating solution is equivalent to approximately 0.005 mg. of mercury. To standardize this solution, add to the standard solution an additional 17 ml. of dithizone solution from buret number two. Shake and draw off this portion. Finally complete the titration by adding dithizone solution in 0.5-ml. portions as previously directed until the end-point is reached. Calculate the amount of mercury in the sample, using the mercury equivalent of the reagent found by titration.

Since the formation of mercury dithizonate takes place slowly, especially near the end of the titration, somewhat better results are claimed by Fischer and Leopoldi<sup>181</sup> by using an indirect method. The mercury solution is extracted with a measured excess of standard dithizone solution, the excess dithizone is then removed by adding a measured excess of standard silver solution, and finally



the excess silver is determined by titrating with the standard dithizone solution. The amount of mercury present is easily determined from the volumes and titers of the standard solutions used.

Winkler<sup>25</sup> has also described a procedure whereby mercury can be determined by the comparative method of Fischer:<sup>181</sup>

**Procedure.** The sample is prepared and extracted as described in the above procedure. Shake the combined extracts with a solution containing 75 ml. of water, 2 ml. of 1:1 sulfuric acid and 4 ml. of 1.5 per cent sodium thiosulfate. Withdraw the chloroform solution and wash the aqueous acid solution with 10 ml. of chloroform. Discard the chloroform solution. By this treatment the mercury is transferred to the aqueous layer as a complex. Place the aqueous solution in a 250-ml. beaker, and add 7-8 ml. of a saturated potassium permanganate solution. Mix, and allow to stand for 8-10 minutes. Add dropwise with stirring a 5 per cent solution of hydroxylamine hydrochloride until the solution is clear, and then add 0.7 ml. in excess. Warm the solution to 53-56° C. and cool. Proceed with the determination of mercury as follows:

To the separatory funnel containing the mercury solution, add sufficient dithizone solution containing 12.5 mg. of dithizone per liter, accurately measured, to give an excess. Shake vigorously for 30 seconds, allow the liquids to separate and withdraw the dithizone solution, along with a little of the acid layer, to a Nessler tube. To a second Nessler tube, which should match the first, add a little dilute sulfuric acid solution, 0.7 ml. of 5 per cent hydroxylamine hydrochloride solution and a volume of dithizone reagent equal to that used in preparing the sample. Add to this Nessler tube from a 10 ml. buret, a standard mercury solution containing 10 $\gamma$  of mercury per ml. Shake frequently during the addition and continue until the color matches that of the unknown. The mercury added is equal to that contained in the unknown.

Alekseev<sup>182</sup> has modified the Fischer<sup>184</sup> method for determining mercury by using a solution of dithizone in sodium pyrophosphate. Mercury can be determined in the presence of other elements capable of color reactions with dithizone due to the masking effect of the pyrophosphate complex compounds formed on adding sodium pyrophosphate to the solutions.<sup>183</sup>

Photometric methods have recently been applied to the determination of small quantities of mercury in various materials. Laug and Nelson<sup>210</sup> have used dithizone for the determination of mercury in such materials as blood, urine, liver, milk powder and cabbage. The important feature of this method is the separation of mercury from copper by shaking the chloroform solution of the dithizonates with an acid potassium bromide solution. In this way mercury is transferred to the aqueous phase in which it is determined by the mixed color method after adjusting the acidity to pH 6. Bismuth does not interfere, even in quantities ranging up to 100 times that of mercury. Silver does not interfere. By this procedure, quantities of mercury ranging from 8 to 90 $\gamma$  have been determined with an accuracy of 92-106 per cent.

**Reagents.** *Dithizone solution:* Dissolve 5.5 g. of purified dithizone in 1 liter of redistilled U.S.P. chloroform.

**Potassium bromide solution:** Purify a 40 per cent (w/v) aqueous solution of potassium bromide as follows: Add 1-2 drops of 6 N sodium hydroxide to 1 liter of the solution, and remove any traces of heavy metals by shaking with small portions of dithizone solution until the last extract remains green. Acidify the aqueous solution very slightly, and remove any dithizone by extracting with chloroform. Make the solution very slightly basic with sodium hydroxide, and store in a Pyrex bottle.

**Buffer solution:** Dissolve 150 g. of disodium hydrogen phosphate and 38 g. of anhydrous potassium carbonate in sufficient distilled water to make 1 liter of solution. Remove any heavy metals by extracting with dithizone, and then extract any dithizone from the aqueous phase with chloroform. Store in a Pyrex vessel.

**Hydroxylamine hydrochloride solution:** Purify a 20 per cent aqueous solution as follows: Shake the solution with 0.1 its volume of a 0.01 per cent solution of dithizone in chloroform. Repeat the extraction several times, using the same volume of dithizone solution, until all heavy metals are removed.

**Procedure.** Transfer 5-25 g. of a sample containing 10-100 $\gamma$  of mercury to a digestion flask, and add slowly from a dropping funnel 30 ml. or more of a 1:1 mixture of concentrated analytical grade nitric and sulfuric acids. Heat gently, but avoid a too vigorous reaction and excessive foaming. Continue the digestion for 2 hours after the greater part of the sample has passed into solution. If charring occurs during the digestion, add occasional small quantities of nitric acid. If flakes of fatty acids separate at the end of the digestion, filter, and use the clear filtrate. When cold, dilute to a suitable volume, and use a 0.1 aliquot for the analysis.

Transfer the aliquot to a 250-ml. separatory funnel containing 50 ml. of 0.25 N hydrochloric acid, and then add 5 ml. of hydroxylamine hydrochloride solution and 10 ml. of dithizone solution. Shake vigorously for 1 minute, and then allow the chloroform to settle. Draw off the chloroform layer into a second 250-ml. separatory funnel containing 50 ml. of 0.25 N hydrochloric acid. Repeat the extraction with a second 10-ml. portion of the dithizone solution, and add the chloroform solution to the second separatory funnel. Shake the latter 30 seconds to wash the chloroform.

Transfer the chloroform solution quantitatively to a third separatory funnel containing 50 ml. of 0.25 N hydrochloric acid, and add 5 ml. of the potassium bromide solution. Shake vigorously for 30 seconds, whereupon the mercury is transferred to the aqueous phase. Draw off and discard the chloroform solution, and wash the aqueous solution with 5-10 ml. of chloroform. Separate the chloroform as completely as possible. To the aqueous solution, add 10 ml. of the buffer solution, and then 10.0 ml. of the dithizone solution. Shake for 1 minute, and allow to stand until the chloroform layer is free of suspended droplets of water. Then transfer the chloroform solution to a suitable absorption cell, cover, and determine the transmittancy at 490 m $\mu$ . The final operations should be carried out in subdued light because of the light sensitivity of mercury dithizonate. A blank should be run.

Reith and van Dijk<sup>209</sup> have described a somewhat longer method for the determination of mercury in biological materials, but in this procedure a colorimetric titration technique is employed for the final determination.

Fischer and Leopoldi<sup>184</sup> report that very small quantities of mercury can be determined in so-called pure metals by a suitable application of the dithizone reaction. The following method may be used for the determination of mercury in zinc:

**Procedure.** Dissolve 2-5 g. of zinc in 20-50 ml. of 1:1 nitric acid and evaporate to a small volume. Add a little hot water and digest the solution with 0.5-1.0 g. of urea. Transfer the resulting solution into a graduated flask, without filtering, and dilute to 100 ml. Neutralize 5 or 10 ml. of this solution with a few drops of ammonium hydroxide until a precipitate is just formed and then make acid to Congo red paper with 1:10 nitric acid. Then add an additional 5 ml. of 1:10 nitric acid, 1-2 drops of silver nitrate solution and about 20 ml. of water. Dilute to 50 ml. and add 6-7 ml. of a green solution of dithizone in carbon tetrachloride and shake vigorously for 30 seconds. Separate the yellow-orange carbon tetrachloride layer, and shake the extract with about 3 ml. of 0.5 N hydrochloric acid. If the color is unchanged, only mercury dithizonate is present, and this can be estimated colorimetrically by any of the usual methods. If an orange-brown color is obtained upon the addition of hydrochloric acid, this is due to the formation of green dithizone liberated from silver dithizonate.

A similar procedure may be used for the determination of mercury in lead, cadmium, bismuth, silver and copper. A mercury content as low as 0.0001 per cent can be determined in zinc, lead, cadmium and bismuth; as low as 0.001 per cent in copper; and 0.1 per cent in silver.

Dithizone has also been used to determine mercury in air<sup>185,186</sup> and in urine.<sup>186</sup>

**Detection and determination of silver.** Dithizone reacts quantitatively with silver in solutions up to 0.5 N in mineral acid to form the keto dithizonate. This compound is soluble in carbon tetrachloride and chloroform to which it imparts a yellow color. In neutral or alkaline solutions, the enol compound is formed. This is red-violet in color, and is practically insoluble in chloroform and carbon tetrachloride. Although this reaction does not appear to have been used analytically, it may possibly be applied to the separation of silver.

It is an interesting fact that silver keto dithizonate is stable in the presence of alkalis, and once formed in an acid solution is not appreciably converted to the enol form, even on shaking the carbon tetrachloride solution with 5 per cent sodium hydroxide. This makes practicable the determination of silver by the mono-color method after removing the excess dithizone from the carbon tetrachloride solution by shaking with dilute ammonia.

Silver may also be determined by the mixed-color technique. In the absence of copper, a dilute solution of dithizone is used as the reagent, and the mixed color varies from green to yellow. If copper is present, a solution of cupric dithizonate is used as the reagent. The mixed color in this reaction varies

from violet to yellow. Using cupric dithizonate, moderate quantities of copper are almost without effect, but with greater quantities of copper, values show a negative error. The use of cupric dithizonate reagent is recommended for general use, since no special purification of acids, distilled water, and other reagents is necessary to remove traces of copper and other metals.

Metals such as lead, zinc, and cadmium, which react with dithizone only in neutral or slightly alkaline solutions, do not interfere unless present in large quantities. Palladium, gold, and mercury must be absent.

Silver may also be determined with dithizone by using an extractive titration procedure.

**The mono-color method.** Fisher and co-workers<sup>48</sup> have developed a mono-color method for the determination of silver. This procedure may be used in the presence of alkali metals, the alkaline earths, magnesium, aluminum, antimony, arsenic, and other metals which do not react with dithizone. Cadmium, lead and zinc do not react with dithizone in an acid solution and do not interfere.

**Reagents.** *Dithizone solution:* Dissolve 5 mg. of purified dithizone in 100 ml. of pure carbon tetrachloride.

*Ammonia wash solution:* Use a 1:1000 ammonia solution which does not impart an appreciable color to the carbon tetrachloride layer when shaken with the dithizone solution.

**Procedure.** Transfer 10 ml. of a solution containing 1-10% of silver to a separatory funnel and acidify with 1 ml. of 4 N nitric or sulfuric acid. Add 5 ml. of dithizone solution, and shake 1-2 minutes. Allow the liquids to separate and draw off the carbon tetrachloride into a second separatory funnel. Repeat the extraction, using successive small portions of dithizone solution until all silver has been removed from the aqueous phase. This point is indicated when the green color of the dithizone solution remains unchanged on shaking with the unknown solution. Finally, wash the aqueous solution with 1-2 ml. of carbon tetrachloride.

Wash the combined carbon tetrachloride extracts 1-2 times with 5-10 ml. of 0.1 N sulfuric acid, and then shake the carbon tetrachloride solution with two 5-ml. portions of the ammonia wash solution. If the last portion of the wash solution is yellowish, repeat the washing. If necessary, remove droplets of water from the carbon tetrachloride solution by filtering through a small filter paper.

Dilute the silver dithizonate solution to a definite volume with pure carbon tetrachloride, and compare the resulting color with that of a standard silver dithizonate solution similarly prepared. If a photometer is used, determine the transmittancy of the solution at 460 m $\mu$ .

Alekseev<sup>182</sup> has modified the method of Fischer<sup>184</sup> for determining small quantities of silver with dithizone by using a solution of dithizone in sodium pyrophosphate instead of in carbon tetrachloride. It is possible to determine silver in the presence of other elements capable of giving color reactions with dithizone, due to the masking effect of the pyrophosphate compounds formed on adding pyrophosphates to solutions of the metal salts.<sup>183</sup>

**The mixed-color method.** In the absence of copper, the following method may be used for the determination of silver: <sup>204</sup>

**Reagents.** *Dithizone solution:* Dissolve 10 mg. of dithizone in 1 liter of redistilled carbon tetrachloride.

*Standard silver solution:* A 0.001 per cent silver solution in 0.1 N sulfuric or nitric acid.

**Procedure.** Adjust the acidity of the sample until it is 0.5 N in sulfuric acid, and transfer 5-20 ml. of the solution to a glass-stoppered, flat-bottomed tube. Add 2.0 ml. of dithizone solution for each 1-5γ of silver. Shake vigorously for 15 seconds and allow the layers to separate. Compare the hue of the carbon tetrachloride solution with that of a series of standards similarly prepared. The colors should be compared against a white background and in good light.

The color may also be compared by means of a colorimetric titration. In this determination, add a standard silver solution to the comparison tube containing the same volume of 0.5 N sulfuric acid and dithizone solution as the unknown. Shake thoroughly after each addition until the color of the carbon tetrachloride solutions match.

The silver content of the carbon tetrachloride solution may also be determined with the aid of a photometer.

In this procedure, shake the acidified silver solution containing up to 25γ of silver with 10.0 ml. of dithizone solution for 30 seconds. Allow the carbon tetrachloride layer to separate and become clear, and transfer to an absorption cell. If the quantity of silver does not exceed 15γ, use 5 ml. of the dithizone solution for greater accuracy. Measure the transmittancy of the solution with the aid of an orange or yellow filter. Prepare a calibration curve by shaking 10.0 ml. of dithizone solution with acidified silver solutions of various concentrations and having approximately the same volume as the unknown.

If copper is present in the unknown, proceed as follows, using cupric dithizonate as the reagent:

**Reagent.** Shake a 0.001 per cent solution of dithizone in carbon tetrachloride with a slight excess of dilute copper sulfate solution in 0.05 N sulfuric acid for 1-2 minutes, and then wash the carbon tetrachloride extract with 0.01 N sulfuric acid to remove droplets of the copper sulfate solution.

**Procedure.** Make the sample solution 0.5 N in sulfuric acid, and transfer 5-20 ml. to a glass stoppered, flat-bottomed tube. Add 2.0 ml. of the cupric dithizonate reagent for each 0.5-5γ of silver, and shake for 2 minutes. Determine the silver content of the solution by the series of standards method or by colorimetric titration.

If the photometer is used, transfer a quantity of the sample containing 2-10γ of silver to a separatory funnel, and shake 2 minutes with 5.0 ml. of the cupric dithizonate solution. Separate the carbon tetrachloride layer, and determine the

transmittancy, using a yellow filter. Prepare a reference curve from standard silver solutions having the same volume and acidify as the unknown.

**The extractive titration method.** Silver may also be determined by an extractive titration method similar to that described above for the determination of lead. With suitable modification, this method may be used for the determination of silver in the presence of lead, zinc, cadmium, arsenic, antimony, bismuth, copper, mercury and gold.

The reaction between silver and dithizone has been used by Fischer<sup>48,62,66,130</sup> for the detection of small quantities of silver. Quantities of silver ranging down to 0.1 $\gamma$  can be detected by this method. Copper, mercury, gold, palladium and other metals capable of forming dithizonates may interfere with this test. By shaking the carbon tetrachloride solution of silver dithizonate that has been washed with 1 per cent sulfuric acid, with a weakly acidified 1 per cent potassium cyanide solution, silver and mercury can be differentiated: if silver dithizonate is present, the yellow color is changed to green, while the color of the mercury compound remains unchanged.<sup>130</sup>

**Detection and determination of copper.** Dithizone reacts with copper in 0.1 mineral acid solution to form the red-violet keto complex. In a slightly ammoniacal or neutral solution the yellowish-brown enol modification is formed.<sup>18</sup> These reactions are used for the detection<sup>62,66,130,137,191</sup> and determination<sup>20,73,138</sup> of copper.

The test for copper can be carried out in the presence of lead, zinc, cadmium and nickel, and is sensitive to about 0.02 $\gamma$  of copper. When the solution containing copper is shaken with a dilute solution of dithizone in carbon tetrachloride, the green color of the reagent is changed to a yellowish-brown. Copper can be detected in the presence of large quantities of other heavy metals and mercury due to the greater tendency toward formation of copper dithizonate as compared to the dithizonates of the other heavy metals.

**Procedure.** Shake a drop of the neutral or weakly ammoniacal solution to be tested with a drop of a solution prepared by dissolving 1-2 mg. of dithizone in 100 ml. of carbon tetrachloride. The green color of the reagent immediately changes to yellow-brown in presence of copper.

This reaction can also be carried out on filter paper or on a spot plate by using a solution containing 10 mg. of dithizone in 100 ml. of carbon tetrachloride. The limit of sensitivity of such a test is approximately 0.2 $\gamma$  of copper.

In acid solutions, palladium, gold, silver and mercury react like copper and must be absent. Bismuth also reacts in acid solution, though less readily than copper.

Dithizone is most frequently used in the determination of copper for the isolation of the metal from acid solutions by a preliminary extraction with a carbon tetrachloride or chloroform solution of the reagent. Useful colorimetric methods, however, have been developed. For high accuracy, the mono-color method cannot be applied, since upon washing the carbon tetrachloride solution of the keto dithizonate with dilute ammonia or other alkaline solution to remove

the excess dithizone a small quantity of the brown enol compound is formed. The mono-color method may be used, however, when the highest accuracy is not required.

According to a procedure developed by Fischer and Leopoldi<sup>78,188</sup> copper can be determined in a manner similar to that used for lead except that instead of adding potassium cyanide the solution is treated with 2 ml. of 10 per cent sulfuric acid for each 10 ml. of copper solution containing 0.3-0.6 $\gamma$  of copper per ml. A large excess of reagent is to be avoided. The excess is eventually removed by treating with dilute ammonium hydroxide, and the violet solution in dilute sulfuric acid is compared with similar solutions containing known quantities of copper.

Mehurin<sup>142</sup> uses dithizone for the determination of copper in foods, but uses sodium pyrophosphate to remove the excess dithizone from the carbon tetrachloride extract, since it has been found that ammonia exercises a bleaching action on solutions containing minute quantities of copper dithizonate. Since the alkalinity of sodium pyrophosphate is quite low, sodium carbonate is added. This method is applicable to 0.0005 mg. of copper.

**Reagents.** *Dithizone solution:* Dissolve 10 mg. of purified dithizone in 100 ml. of carbon tetrachloride.

*Pyrophosphate-carbonate solution:* Dissolve 12 g. of recrystallized sodium pyrophosphate and 0.5 g. of sodium carbonate in water and dilute to 200 ml. Add about 50 ml. of the dithizone solution and shake in a separatory funnel. Separate and discard the carbon tetrachloride layer, and shake the aqueous layer with successive 50-ml. portions of dithizone solution until only a trace of pink color is extracted. Extract the aqueous layer with three 50-ml. portions of amyl alcohol to remove dithizone, and then extract with two 50-ml. portions of carbon tetrachloride to remove the amyl alcohol.

**Procedure.** Ash a suitable sample of organic matter in a silica dish in a muffle at a temperature not exceeding 500° C. Dissolve the ash in 1:3 hydrochloric acid, using heat if necessary, and dilute to a definite volume with water.

Transfer a 10-ml. sample containing not more than 0.005 mg. of copper to a separatory funnel, and neutralize to methyl orange with 1:3 ammonium hydroxide. Add 2 drops of concentrated nitric acid, 1 ml. of the dithizone solution, and 2 ml. of carbon tetrachloride. Shake well, and carefully separate the carbon tetrachloride layer so as not to include any of the aqueous solution. Extract with 5-10 ml. of water containing 2-3 drops of concentrated hydrochloric acid. Again separate the carbon tetrachloride layer and wash.

Add 5 ml. of the pyrophosphate-carbonate solution and 5 ml. of water to the carbon tetrachloride solution, and shake 30 seconds. Separate carefully, and compare the color of the carbon tetrachloride layer with that of a series of standards similarly prepared. The standards should contain 0.000, 0.0005, 0.001, 0.002, 0.003, 0.004 and 0.005 mg. of copper.

Tin should be removed before applying this procedure.

Excellent results are obtained in testing so-called pure lead, zinc, cadmium, nickel, cobalt, aluminum, arsenic, antimony, tin and compounds of these elements.

Numata and Matukawa<sup>139</sup> have used the following method for the micro-colorimetric determination of copper.

**Reagent.** Dissolve 10 mg. of dithizone in 50 ml. of carbon tetrachloride and transfer to a separatory funnel. Add an equal volume of 1:200 ammonium hydroxide solution and shake vigorously. Withdraw the carbon tetrachloride and add 50 ml. of pure carbon tetrachloride to the aqueous solution. Now add 25 ml. of 1 per cent sulfuric acid and again shake. Wash the carbon tetrachloride solution several times with water, and store in a brown bottle under 25 ml. of 12 per cent sodium sulfite in N sulfuric acid.

**Procedure.** Measure 1 ml. of solution containing less than 6γ of copper into a small separatory funnel and dilute to 5 ml. with water. Add 1 ml. of 10 per cent sulfuric acid and 3 ml. of dithizone reagent and shake for 5 minutes. If less than 4γ of copper is present, the solution is colored dark green, and with 6γ of copper the color is dark violet. A reddish-violet color, however, indicates that an excess of copper is present. Transfer the carbon tetrachloride solution quantitatively to a separatory funnel and shake two minutes with 4 ml. of 1:200 ammonium hydroxide, and discard the latter. Repeat the washing 7 times and finally add 5 ml. of 1 per cent sulfuric acid to the carbon tetrachloride solution and shake for 1 minute. Filter the violet-colored solution and measure in a photometer, or compare with standards similarly prepared.

van Duuren<sup>114</sup> has used a similar procedure, but has measured the color of the dithizonate in a Lovibond tintometer against definite units of red, yellow, and blue. By reference to a diagram prepared from standard solutions the amount of copper contained in the solution can be estimated.

Muller and Burtzell<sup>141</sup> claim that the dithizone method for copper is less satisfactory than the dithiocarbamate and the salicylate methods.

The mixed-color method gives good results. The aqueous solution should not be more than 0.05-0.1 N in hydrochloric acid, especially if the excess of dithizone is small. It is important that the carbon tetrachloride used be pure, since otherwise the reaction between copper and dithizone in acid solution is very slow. The following procedure illustrates the mixed-color method:<sup>204</sup>

**Reagents.** *Dithizone solution:* Dissolve 10 mg. of dithizone in 1 liter of reagent quality carbon tetrachloride.

*Standard copper solution:* Dissolve 0.1964 g. of clear uneffloresced crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in water, add sufficient hydrochloric or sulfuric acid to make the final acid concentration 0.1 N, and then dilute to 500 ml. This solution has a concentration of 0.01 per cent. Prepare a 0.002 per cent solution by diluting with 0.1 N hydrochloric acid.

**Procedure.** Adjust the acidity of 10 ml. of the sample containing about 5γ of copper to 0.05-0.1 N in hydrochloric or sulfuric acid, and add 5.0 ml. of the 0.001 per cent dithizone solution from a covered buret or pipet. Shake the mixture for 2 minutes in a small separatory funnel. If the color of the carbon tetrachloride solution is red-violet, add an additional 5-ml. portion of the reagent,



or less, and again shake. The color of the solution must differ from that of the original dithizone solution.

Separate the carbon tetrachloride solution and transfer to a suitable cell. Cover to prevent evaporation, and measure the transmittancy at  $510m\mu$  or  $625m\mu$ . The solution must be perfectly clear. Prepare a reference curve from copper sulfate solutions of approximately the same volume and acidity as the sample solution.

The final determination may also be carried out by the standard series method. A suitable mixed color is obtained by adding 5 ml. of 0.001 per cent dithizone solution to a sample containing 1-4 $\gamma$  of copper. In the lower part of this range, however, more accurate results are obtained by using a smaller volume of dithizone solution. If the approximate concentration of copper is not known, it is good practice to add only 0.5-1 ml. of dithizone, shake, and then add an additional quantity of the reagent, if necessary, until a suitable mixed color is obtained.

Grubitsch and Sinigoj<sup>140</sup> have used a mixed-color titration and report that the error is large in the green and reddish-violet range, but that it may be reduced to about 2 per cent when the color is gray.

Assaf and Hollibaugh<sup>148</sup> have successfully applied the extractive titration technique to the determination of copper in mineral oils. The procedure used is similar to that employed by Wilkins and co-workers<sup>49</sup> for the determination of lead in biological materials.

It has been explained previously that dithizone is most frequently employed in copper determinations for the isolation of the metal as a preliminary to the final determination by various methods. In addition to copper, other metals which react with dithizone in 0.1-1 N mineral acid solution are gold, silver, palladium, mercury and bismuth. Bismuth reacts only incompletely when a moderate excess of dithizone is used in the extraction. The use of alkali halides or halogen acids as precipitants and complex formers makes possible the separation of copper from silver, mercury and bismuth. Mercuric mercury does not react with dithizone in a bromide solution of pH 1, due to the formation of the slightly ionized  $HgBr_4^-$  ion. Laug and Nelson<sup>210</sup> have used this principle for the separation of copper from small amounts of mercury. This is accomplished by shaking 20 ml. of a chloroform solution of the dithizonates of copper and mercury with 5 ml. of a 40 per cent potassium bromide solution and 50 ml. of 0.25 N hydrochloric acid. Copper remains in the chloroform layer while mercury passes into the aqueous phase. Any bismuth which is extracted along with copper from the acid solution is removed from the organic solvent layer by shaking the latter with an equal volume of 2 per cent potassium iodide solution in 0.01 N hydrochloric acid.<sup>144</sup> The aqueous phase is then shaken with 5-10 ml. of 0.001 N dithizone solution to recover any copper which may have been transferred to it.

Greenleaf<sup>144</sup> eliminates interference by bismuth by extracting the solution containing copper and bismuth dithizonates with an acidified potassium iodide solution. Bismuth is removed as the iodide complex. The remainder of the procedure includes the oxidation of the copper dithizonate with bromine in 5 per cent sulfuric acid, and extraction of copper from the carbon tetrachloride layer

to the aqueous layer. The aqueous solution is then digested with nitric and perchloric acids and the copper determined by the carbamate method.

Bismuth, if present in the sample, accompanies copper. These two metals may be separated as follows:

**Procedure.** If copper and bismuth have been separated from the original solution, wash the dithizone extract with 20 ml. of 0.01 N hydrochloric acid to remove any zinc, and then remove the excess dithizone from the extract with 0.02 N ammonium hydroxide. Extract the copper and bismuth from the chloroform by shaking with 1 per cent nitric acid. Neutralize the acid solution with sodium hydroxide and add sufficient tartaric acid to make the solution 0.5 N, and again extract with dithizone. This time the copper is extracted with only very small quantities of bismuth. The bismuth may be separated from the copper by extracting the copper with dithizone from a solution of both in 0.5 N hydrochloric acid. Bismuth remains in the acid aqueous phase. It is difficult, however, to extract copper completely from 0.5 N hydrochloric acid, and several extractions are therefore necessary. The copper extract is finally washed free of dithizone with 0.02 N ammonia, and then determined by brominating the organic part of the molecule and titrating iodometrically. For the details of this procedure, see section on zinc (page 534).

The effect of pH and dithizone concentration on the extraction of copper and bismuth is shown in Table 102. The metal contained in 25 ml. of an aqueous solution was shaken with 25 ml. of carbon tetrachloride of calculated composition.

Fischer<sup>10</sup> indicates that it is possible to separate copper from nickel and cobalt by extracting with a solution of dithizone at pH below 4-5.

Hibbard<sup>40</sup> recommends isolating copper from an acid solution of pH 1-4 by repeated extraction with dithizone in chloroform.

Sandell<sup>26</sup> has used dithizone for the determination of copper, zinc and lead in silicate rocks. The separation of copper, zinc and lead from most other constituents of the sample is effected by extracting with dithizone in carbon tetrachloride from a citrate solution containing a slight excess of ammonia. The pH should be approximately 8.5. The extraction of zinc and lead from such a solution is virtually complete with an excess of the reagent. When a solution of the keto forms of copper, zinc and lead dithizonate is shaken with approximately 0.01 N hydrochloric acid, the copper complex remains virtually unchanged in carbon tetrachloride, but the zinc and lead complexes are decomposed. The zinc and lead can thus be recovered quantitatively from a carbon tetrachloride solution, even in the presence of an excess of the reagent. It is important that copper be present as the keto and not the enol complex. An excess of carbon tetrachloride must be present to combine with any copper ions liberated by the acid treatment.

After the extraction of copper with dithizone it is necessary to destroy the cupric dithizonate and excess dithizone in the extracts before proceeding with the final determination. This may be effected by evaporating the organic solvent and heating the residue with a mixture of sulfuric and perchloric acids until a completely colorless solution is obtained.<sup>27</sup> Another method is to evaporate the

carbon tetrachloride solution to dryness in a silica dish, evaporate the residue to copper oxide, and dissolve the oxide in hydrochloric acid. This method is the more rapid but may give slightly low results.

TABLE 102.—EFFECT OF pH AND CONCENTRATION OF DITHIZONE ON EXTRACTION OF COPPER AND BISMUTH

EXTRACTION OF COPPER			
pH	Excess Reagent		
	None	50 Per Cent	650 Per Cent
	25γ Cu—Per Cent Copper Extracted		
—0.6	0	0	41
—0.4	11	16	85
0.2	60	72	100
1.2	89	100	100
2.2	100	100	...
3.2	100	100	...

EXTRACTION OF BISMUTH			
pH	Excess Reagent		
	None	100 Per Cent	900 Per Cent
	250γ Bi—Per Cent Extracted		
0.2	0	0	0
1.2	12	48	100
2.2	48	87	100

Greenleaf<sup>148</sup> states that copper can be recovered quantitatively from the chloroform extract of copper dithizonate by shaking with 6 N hydrochloric acid, or by oxidizing dithizone with bromine and shaking with 1 N hydrochloric acid.

In the presence of small quantities of silver, mercury and bismuth, the determination may be carried out without a preliminary extraction of copper by the method of Bendix and Grabenstetter.<sup>149</sup> They extract a sample solution of pH 2 (containing a phosphate-citric acid buffer) with a measured volume of 0.0015 per cent dithizone solution in carbon tetrachloride, and then shake the extract with a 2 per cent solution of potassium iodide in 0.01 N hydrochloric acid to decompose the dithizonates of silver, bismuth and mercury. By this treatment, copper is left alone in the carbon tetrachloride layer, in which it is determined photometrically.

Dithizone has been used for the determination of copper in plants and biological materials; <sup>92,93,145-147,186</sup> in oil; <sup>20,148</sup> in milk and other foods; <sup>27,149,194</sup> in refined zinc; <sup>150</sup> in ballistic tests; <sup>151</sup> nickelplating baths; <sup>198</sup> soil.<sup>186</sup>

**Detection and determination of cobalt.** When a solution containing 1-2 mg. of dithizone in 100 ml. of chloroform is shaken with a 2 per cent ammoniacal solution containing cobalt, a reddish-violet color is obtained with as little as 0.04 $\gamma$  of cobalt. This test may be carried out in the presence of nickel. If zinc is present, use a 2 per cent sodium hydroxide solution. The color is first bluish-violet and fades to a nearly colorless gray.<sup>62,152,191</sup>

Fischer <sup>153</sup> has also used an ammoniacal solution of dithizone as a very sensitive reagent for cobalt. A very dilute cobalt solution is colored reddish-violet by an ammoniacal solution of dithizone. The reagent is prepared by adding dithizone to 1:10 ammonia until the color corresponds to that of methyl orange which is used as an indicator. The keeping qualities of this solution are greatly improved by adding a small quantity of hydrazine sulfate. Nickel does not interfere. Potassium cyanide interferes and metals precipitated by ammonium hydroxide must be removed. In the absence of cobalt, nickel colors the reagent an olive green. Zinc gives a similar color, but this interference is eliminated by use of the reagent in sodium hydroxide and a sodium hydroxide solution of cobalt. Copper must be removed.

Sandell and Perlich <sup>88</sup> have used dithizone in a procedure for the determination of cobalt in silicate rocks. This determination is based on the extraction of cobalt with a carbon tetrachloride solution of dithizone from an ammoniacal citrate solution of the sample. The carbon tetrachloride solution, which also contains the dithizonate of copper, zinc, lead and some nickel, is evaporated to dryness and the residue is ignited to destroy organic matter. The residue of oxide is dissolved in aqua regia. The copper is reduced with stannous chloride, and cobalt is then determined colorimetrically with ammonium thiocyanate and acetone.

Marston and Dewey <sup>154</sup> have used dithizone for the extraction of cobalt in plant and animal tissues.

Hibbard <sup>46</sup> has used dithizone for the isolation of zinc, copper and cobalt as a preliminary to a bromometric titration procedure. Copper and bismuth, if present, are removed from an acid solution of pH 1-4 by repeated extraction with dithizone in chloroform. After the removal of copper and bismuth, the pH of the aqueous solution is adjusted to 7-9 (phenol red) and zinc and other metals, such as lead, cobalt, nickel and cadmium are extracted with dithizone in chloroform. The excess reagent is removed and zinc, including lead and cadmium if present, are separated from cobalt by extracting three or more times successively with 20-30-ml. portions of 0.01 N hydrochloric acid. The process is repeated once or twice more if the quantity of copper is large. By again making the acid extract alkaline, the metal is recombined with dithizone as originally described, and again extracted with 0.01 N hydrochloric acid. Zinc, lead and cadmium pass into the acid solution, while cobalt and most of the nickel remain in the chloroform. The solution is washed free of excess reagent with ammonia, and cobalt determined by a bromine titration as described on page 534.

**Detection and determination of zinc.** **Detection of zinc.** Dithizone reacts with zinc in neutral, alkaline and acetic acid solutions to form a purple-red dithizonate which dissolves in carbon tetrachloride without change in color. This reaction has been proposed by Fischer<sup>23,62</sup> as a sensitive test for zinc. In neutral solution as little as 0.025% of zinc can be detected. Many metals interfere by forming colored dithizonates, but various methods have been proposed for eliminating this interference. Silver, copper, mercury, gold, bismuth, cadmium and lead are masked by treating with sodium thiosulfate, and potassium cyanide in a faintly acid solution eliminates interference by cobalt, nickel and palladium. The colors produced with zinc, cobalt, nickel and palladium can also be distinguished by the difference in the behavior toward ammonium sulfide reagent. By combining the effects of sodium thiosulfate and potassium cyanide, and by oxidizing any stannous tin, it is possible to detect zinc with dithizone in the presence of any other metal.<sup>23</sup>

Reinacker and Schiff<sup>155</sup> propose carrying out the test in an alkaline solution.

**Reagent.** Dissolve 10 g. of dithizone in 100 ml. of carbon tetrachloride.

**Procedure.** To a few drops of the solution to be tested, add 0.5 ml. of 2 N sodium hydroxide and 0.5 ml. of dithizone solution and shake vigorously. If cadmium, copper or mercury are present, first treat the solution with hydrogen sulfide in the presence of acid, filter, and then test the filtrate.

Fischer and Leopoldi<sup>156</sup> state that the test proposed by Reinacker and Schiff<sup>155</sup> is less specific than under other conditions. Cadmium, copper, mercury, nickel, cobalt, gold and palladium interfere. Ammonium salts also cause trouble, and sometimes a negative test is obtained when zinc is actually present. The use of an acetate-buffered solution is recommended, since this permits the use of the test in the presence of nickel, cobalt and cadmium. If copper, mercury, silver, gold or palladium is present, the solution can be reduced with hypophosphorus acid, and in this way the test made very generally applicable.<sup>156</sup>

Vanossi<sup>157</sup> suggests making the zinc test as follows:

**Procedure.** Treat 0.1-0.3 ml. of an acid solution of dithizone with ether and ammonium thiocyanate to form an ether solution of zinc thiocyanate, and then treat successively with solutions of ammonium fluoride and sodium sulfite to remove other cations. Separate the ether layer and treat with potassium cyanide solution until it is permanently decolorized. Then add 1 drop of thiocyanate solution and 1 drop of acetic acid. Again separate the ether layer, and add to an ammoniacal solution of dithizone in the presence of carbon tetrachloride, and follow with a drop of sodium sulfide solution. A pure red color in the two phases indicates the presence of zinc. This test is said to be sensitive to 0.02% of zinc.

Dobbins and Southern<sup>158</sup> have used dithizone for detecting zinc in a systematic scheme of analysis. Wenger<sup>159</sup> and co-workers have studied the use of dithizone for the detection of zinc and recommend its use, although they point out that many ions interfere.

**Determination of zinc.** Fischer<sup>23,137</sup> has recommended the use of dithizone for the determination of zinc. Dithizone reacts with zinc in weakly alkaline solutions to form the keto complex, which is soluble in chloroform and carbon tetrachloride, and to which it imparts a bright red color. Many other metals react under the same conditions as zinc, but this interference may be eliminated by the use of suitable complex formers. At pH 4-5.5 sodium thiosulfate largely prevents the reaction with bismuth, cadmium, copper, gold, lead, mercury and silver, although it does not interfere with the formation of zinc dithizonate.<sup>23</sup> Potassium cyanide is used if much nickel and cobalt are present. Sodium diethyldithiocarbamate is also used as a general complex former in ammoniacal solutions in the zinc determination after the removal of copper.<sup>164,165</sup> Only small amounts of cadmium may be present if this reagent is used.

Zinc may be determined either by the mono-color or the mixed-color method. The mixed-color method is preferable if only traces of other metals which react with dithizone are present, so that only a little thiosulfate need be added. A high concentration of thiosulfate reduces the sensitivity of the mixed-color method, since a weak zinc thiosulfate complex is formed. If high concentrations of interfering metals are present, the mono-color method is the more satisfactory.

**The mono-color method.** Traces of zinc may be determined in the presence of large quantities of such metals as iron, lead and silver by a mono-color method proposed by Fischer and Leopoldi.<sup>23</sup> The determination is more difficult in the presence of bismuth, copper and mercury, because of the relatively large quantities of thiosulfate necessary to prevent the reaction of dithizone with these metals, but it is possible to determine 10 $\gamma$  of zinc in the presence of 10 mg. of these metals. Not more than 0.1 mg. of cadmium may be present. Stannous tin interferes, but stannic tin does not. Large quantities of tin may be eliminated by volatilization as the bromide.

The excess dithizone is removed from the reaction mixture by washing with a solution of sodium sulfide instead of ammonia or other base, since traces of zinc in the sulfide solution do not react with the excess dithizone. Ammonia and other bases commonly contain zinc as an impurity, and may therefore cause error unless especially purified. The carbon tetrachloride extract of zinc dithizonate is washed with a sodium thiosulfate solution before removing the excess dithizone in order to decompose the traces of other metal dithizonates that might be present.

**Reagents.** *Dithizone solution:* Dissolve 50 mg. of dithizone in 1 liter of pure carbon tetrachloride.

*Sodium acetate solution:* Purify a 0.5 M of sodium acetate by shaking with successive small portions of 0.005 per cent dithizone solution. Filter through a small moistened paper to remove drops of carbon tetrachloride.

*Sodium thiosulfate solution:* Dissolve 50 g. of sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , in 100 ml. of water.

*Sodium thiosulfate wash solution:* Mix 225 ml. of 0.5 M sodium acetate solution, 10 ml. of 50 per cent sodium thiosulfate solution, and 40 ml. of 10 per

cent nitric acid, and then dilute to 500 ml. with water. Remove traces of zinc by shaking with dithizone solution.

*Sodium sulfide wash solution:* Dilute 40 ml. of a 1 per cent sodium sulfide solution with 1 liter of water.

**Procedure.** The acidity of the sample should be adjusted to 0.1 N in hydrochloric acid. If the solution is more strongly acid, evaporate in a silica dish. Neutralization of the acid usually causes error, since most bases contain traces of zinc as an impurity. To 10-25 ml. of a solution containing 5 $\gamma$  of zinc, add the sodium acetate solution until the pH is 5-5.5 as indicated by bromocresol green. Then add sufficient sodium thiosulfate to form complexes with the interfering metals. The quantity of thiosulfate added depends on the kind and amount of foreign metal present. The quantity of thiosulfate required for each mg. of foreign metal is obtained from Table 103.

TABLE 103.

Metal	g. of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per mg. of Metal
Mercury .....	0.65 -0.75
Copper .....	0.5 -0.6
Bismuth .....	0.3 -0.35
Silver .....	0.05 -0.06
Lead .....	0.032-0.04

Add 2-3 ml. of the dithizone solution and shake vigorously for 1 minute. Draw off the carbon tetrachloride solution into a second separatory funnel, and wash the aqueous solution with 0.5-1 ml. of carbon tetrachloride. Again extract the solution with dithizone, and repeat the extraction until the last portion does not undergo change in color after shaking 2-3 minutes.

Combine the carbon tetrachloride extracts, and wash 2-3 times with 5-ml. portions of the sodium thiosulfate wash solution. Then wash once with water, and 2-3 times with 5-ml. portions of the sodium sulfide solution. The last portion of the sodium sulfide wash solution must remain colorless.

Dilute the zinc dithizonate solution to a definite volume with carbon tetrachloride, and determine the transmittancy of the solution at 535  $m\mu$ , or compare with a standard similarly prepared. Run a blank through all steps of the procedure.

The effect of foreign metals on the determination of zinc by the mono-color method is shown in Table 104, which is taken from the work of Fischer and Leopoldi.<sup>23</sup>

**The mixed-color method.** The mixed-color method is always preferred to the mono-color method when large quantities of metals which react with dithizone are absent.<sup>204</sup> It is especially suitable for the determination of zinc in rocks, biological materials and water. Lead is practically without effect in

this method, although copper must not be present in quantities exceeding two times that of zinc. Nickel, bismuth and cadmium also interfere somewhat. The concentration of zinc dithizonate in the carbon tetrachloride solution may be found directly by measuring the transmittancy with a green filter, or indirectly by determining the excess dithizone by measuring the transmittancy with a red filter. The determination may also be made by the series of standards method.

TABLE 104.—DETERMINATION OF ZINC WITH DITHIZONE

Foreign Metal	Zn Taken $\gamma$	Zn Found $\gamma$	Error $\gamma$
	6.2	6.0	-0.2
	4.1	4.1	0.0
	37.4	36.8	-0.6
Fe (III) 50 mg. ....	6.2	7.3	+1.1
Mn 100 mg. ....	6.2	6.3	+0.1
Cu 10 mg. ....	8.3	8.8	+0.5
Ag 100 mg. ....	16.6	16.2	-0.4
Pb 125 mg. ....	8.3	8.7	+0.4
Cd 0.07 mg. ....	12.4	12.8	+0.4
Sn <sup>a</sup> 150 mg. ....	16.6	16.9	+0.3
Al <sup>b</sup> 100 mg. ....	6.2	7.0	+0.8
Ni <sup>c</sup> 100 mg. ....	6.3	6.0	-0.3
Co <sup>c</sup> 100 mg. ....	6.4	6.8	+0.4

<sup>a</sup> Sn volatilized with Br<sub>2</sub> + HBr.

<sup>b</sup> Double extraction.

<sup>c</sup> In the presence of KCN.

**Reagents.** *Dithizone solution:* Dissolve 10 mg. of dithizone in 1 liter of pure carbon tetrachloride.

*Acetate buffer:* Mix equal volumes of 2 N sodium acetate and 2 N acetic acid, and purify the mixture by extracting any heavy metals with the dithizone solution. Filter through a small dry filter to remove any droplets of carbon tetrachloride. The pH of the solution is about 4.75.

*Sodium thiosulfate solution:* Dissolve 25 g. of sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O, in 100 ml. of water.

*Standard zinc solution:* Prepare a 0.001 per cent zinc solution in 0.01-0.02 N HCl.

**Procedure.** Adjust the acidity of the sample solution to 0.01-0.03 N, and transfer a 10-ml. portion containing 5 $\gamma$  or less of zinc to a separatory funnel. Add 5.0 ml. of the acetate buffer and 1.00 ml. of the thiosulfate solution. Mix well, add 5.0 ml. of the dithizone solution, and shake vigorously for 2 minutes. Dry the stem of the funnel with filter paper, and draw off the clear carbon tetrachloride solution into a cell and cover to prevent evaporation. Determine the transmittancy of the solution with light of wave length 520-540 m $\mu$  or 620 m $\mu$ . The amount of zinc present is determined by reference to a standard curve. The comparison may be made by the series of standards method.



Sandell<sup>26</sup> has used dithizone for the determination of small quantities of zinc in silicate rocks. Copper, zinc and lead are separated from most other constituents of rock by carrying out a dithizone-carbon tetrachloride extraction in a citrate solution containing a slight excess of ammonia. The pH of the solution is adjusted to approximately 8.5. The extraction of lead and zinc from such a solution is virtually complete with an excess of the reagent.

Grubitsch and Sinigoj<sup>140</sup> have used a mixed-color titration technique for determining zinc. van Duuren<sup>114</sup> has determined small quantities of zinc with dithizone with the aid of a Lovibond tintometer. Stout and co-workers<sup>160</sup> have used a polarographic method for estimation of zinc in the presence of nickel, cobalt, cadmium, lead, copper and bismuth in plant materials.

Lang<sup>44,45</sup> has extracted zinc with dithizone and made the final determination with potassium ferricyanide and potassium iodide.

Walkley<sup>162</sup> has studied the extraction of zinc with dithizone from ammoniacal solutions and recommends extraction from a solution of pH 9.8.

Ritchie and co-workers<sup>163,164</sup> have studied the use of diethyldithiocarbamate in the determination of zinc with dithizone. They extract all possible interfering metals as the carbamates and dithizonates with carbon tetrachloride from aqueous solutions that are too strongly acid for the extraction of zinc, and they then fix the remaining interfering metals other than zinc with diethyldithiocarbamate in a weakly alkaline solution. Dithizone appears to be almost specific as a test for zinc under these conditions. Cowling and Miller<sup>165</sup> have used this principle for the determination of small quantities of zinc in plant material. Zinc can be quantitatively extracted as the dithizonate from aqueous solutions at a pH of 8-9 with carbon tetrachloride containing an excess of dithizone, but in the presence of carbamate complete extraction of the zinc dithizonate cannot be effected. Cowling and Miller<sup>165</sup> have, however, worked out a procedure for the determination of traces of zinc in plant materials in which carbamate is used to eliminate interference of other metals which also form dithizone complexes. The following procedure is taken directly from the published work of Cowling and Miller:<sup>165</sup> \* Most of the necessary reagents contain appreciable amounts of zinc and other metals that form dithizone complexes, and these must be removed if high accuracy is expected. Chemicals of the highest grade should be used and purified as follows:

*Standard zinc solutions:* Stock solution (1000 micrograms of zinc per ml.). Place 0.25 gram of pure zinc in a 250-ml. volumetric flask. Add about 50 ml. of water and 1 ml. of concentrated sulfuric acid, then heat on the steam bath until all zinc is dissolved. Dilute to 250 ml. and store in a pyrex vessel.

Standard solution (10 micrograms of zinc per ml.). Dilute 10 ml. of the above stock solution to 1 liter. Store in a pyrex vessel.

*N ammonium hydroxide solution:* Distill into water one-half volume of concentrated ammonium hydroxide by use of an all-pyrex glass distillation apparatus, then dilute to the proper concentration. Store in a glass-stoppered pyrex vessel.

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*N hydrochloric acid:* Displace hydrogen chloride gas from a volume of concentrated hydrochloric acid in a pyrex flask by the slow addition of an equal volume of concentrated sulfuric acid by means of a dropping funnel which extends below the surface of the concentrated hydrochloric acid. Absorb the displaced hydrogen chloride gas by conducting it by means of a delivery tube to the surface of a volume of water. No heat is necessary. Dilute to the proper concentration. One hundred and fifty milliliters of each of the acids will yield 1 liter of purified hydrochloric acid solution of a concentration greater than normal.

*Dithizone reagent:* Dissolve 0.20 gram of diphenylthiocarbazon in 500 ml. of carbon tetrachloride and filter the solution to remove insoluble matter. Place the solution in a glass-stoppered bottle or large separatory funnel, add 2 liters of 0.02 N ammonia (40 ml. of N ammonia diluted to 2 liters), then shake to extract the dithizone into the aqueous phase. Separate the phases, discard the carbon tetrachloride phase, and extract the ammoniacal solution of dithizone with 100-ml. portions of carbon tetrachloride until the carbon tetrachloride extract is a pure green color. Discard the carbon tetrachloride phase after each extraction. Add 500 ml. of carbon tetrachloride and 45 ml. of N hydrochloric acid and shake to extract the dithizone into the carbon tetrachloride. Separate the phases and discard the aqueous phase. Dilute the carbon tetrachloride solution of dithizone to 2 liters with carbon tetrachloride. Store the dithizone reagent in a brown bottle in a dark cool place.

*Ammonium citrate solution:* (0.5 molar.) Dissolve 226 g. of ammonium citrate,  $(\text{NH}_4)_2\text{HC}_6\text{H}_6\text{O}_7$ , in 2 liters of water. Add concentrated ammonia (80-85 ml.) until the solution has a pH of 8.5 to 8.7. Add an excess of dithizone reagent (orange-yellow coloration in aqueous phase after shaking and separation of phases), and extract with 100-ml. portions of carbon tetrachloride until the extract is a full green color. Add more dithizone if necessary. Separate the aqueous phase from the carbon tetrachloride and store in a pyrex vessel.

*Carbamate reagent:* Dissolve 0.25 g. of sodium diethyldithiocarbamate and dilute to 100 ml. with water. Prepare a fresh solution just before use.

Now prepare three solutions as follows:

*Solution A:* Dilute 1 liter of 0.5 M ammonium citrate and 140 ml. of N ammonium hydroxide to 4 liters.

*Solution B:* Dilute 1 liter of 0.5 M ammonium citrate and 300 ml. of N ammonium hydroxide to 4.5 liters. Just before use, add 1 volume of freshly prepared carbamate reagent to 9 volumes of the ammonia-ammonium citrate solution to obtain the volume of Solution B immediately required.

*0.02 N Hydrochloric acid:* Dilute 100 ml. of N hydrochloric acid to 5 liters.

*Preparation of sample:* Ash a 5 g. sample of the finely ground, air-dry plant material in a platinum dish in an electric muffle at 500° C. to 550° C. Wet the ash with a little distilled water, then add 10 ml. of N hydrochloric acid (more if necessary) and heat on a steam bath until all substances soluble in hydrochloric

acid are brought into solution. Add 5 or 10 ml. of hot water. Filter off the insoluble matter on a 7-cm. filter paper (Whatman No. 42 or equivalent) which has been previously washed with two 5-ml. portions of hot N hydrochloric acid, then washed with hot water until free of hydrochloric acid, and collect the filtrate in a 100-ml. volumetric flask. Wash the filter with hot water until washings are no longer acid to methyl red. Add a drop of methyl red indicator to the filtrate in the 100-ml. flask, add N ammonium hydroxide until neutral to methyl red, then add 4 ml. of N hydrochloric acid. Allow the contents of the flask to cool, then make to volume with water.

*Extraction* (separation of dithizone complex-forming metals from the ash solution). Pipet an aliquot of the ash solution, containing not more than 30 micrograms of zinc into a 125-ml. Squibb separatory funnel. Add 1 ml. of 0.2 N hydrochloric acid for each 5 ml. of ash solution less than 10 ml. taken, or 1 ml. of 0.2 N ammonium hydroxide for each 5 ml. over 10 ml. taken. A 10-ml. aliquot has usually been found satisfactory in the analysis of plant materials. Add 40 ml. of Solution A and 10 ml. of dithizone reagent. Shake vigorously for 0.5 minute to extract from the aqueous phase the zinc and other dithizone complex-forming metals which may be present, then allow the layers to separate. At this point an excess of dithizone, which is indicated by an orange or yellow-orange coloration of the aqueous phase, must be present. If excess dithizone is not present, add more of the reagent until after shaking an excess is indicated.

Shake down the drop of carbon tetrachloride extract from the surface, and draw off the carbon tetrachloride extract into a second separatory funnel as completely as possible without allowing any of the aqueous layer to enter the stopcock bore. Rinse down the carbon tetrachloride extract from the surface of the aqueous layer with a 1- to 2-ml. portion of clear carbon tetrachloride, then run off this carbon tetrachloride into the second funnel without permitting the aqueous phase to enter the stopcock bore. Repeat this rinsing process as many times as is necessary to flush the extract completely into the second funnel. Add 5 ml. of clear carbon tetrachloride to the first funnel, shake 0.5 minute, and allow the layers to separate. The carbon tetrachloride layer at this point will have a clear green color if metals which form dithizone complexes have been completely extracted from the aqueous phase by the previous extraction. Run off the carbon tetrachloride layer into the second funnel, then flush down the extract from the surface and out of the funnel as was done before. If the last extract does not possess a distinct clear green color, repeat the extraction with a 5-ml. portion of clear carbon tetrachloride and the flushing out process until complete extraction of the dithizone complex-forming metals is assured, then discard the aqueous phase.

Pipet 50 ml. of 0.02 N hydrochloric acid into the separatory funnel containing the carbon tetrachloride solution of metal dithizonates. Shake vigorously for 1.5 minutes, then allow the layers to separate. Shake down the drop from the surface of the aqueous phase, and run off as completely as possible the carbon tetrachloride phase, which contains all the copper as dithizonate, without allowing any of the aqueous phase, which contains all the zinc, to enter the stopcock bore.

Rinse down the carbon tetrachloride extract from the surface of the aqueous phase and rinse out the stopcock bore with 1- to 2-ml. portions of clear carbon tetrachloride (in the same manner as was done in the first extraction) until all traces of green dithizone have been washed out of the funnel. Shake down the drop of carbon tetrachloride from the surface of the aqueous phase, and run off the carbon tetrachloride as completely as possible without allowing any aqueous phase to enter the stopcock bore. Remove the stopper from the funnel and lay it across the neck of the funnel until the small amount of carbon tetrachloride on the surface of the aqueous phase has evaporated.

Pipet 50 ml. of Solution B and 10 ml. of dithizone reagent into the 50 ml. of 0.02 N hydrochloric acid solution. Shake for one minute, then allow the phases to separate. Flush out the stopcock and stem of the funnel with 1 ml. or so of the carbon tetrachloride extract, then collect the remainder in a test tube. Pipet 5 ml. of the extract into a 25-ml. volumetric flask and dilute to the mark with clear carbon tetrachloride, and then determine the per cent light transmission of the diluted solution with a photoelectric colorimeter, equipped with a Sextant green (Corning No. 401) filter, or equivalent. Readings should be taken not later than 2 hours after the final extraction. Protect extracts from light as much as possible.

A blank determination must be run with each series of zinc determinations in order to determine the correction to be applied for the zinc present in the hydrochloric acid and ammonium hydroxide in the ash solution and the zinc picked up by the other reagents from their containers since the determination of the standard curve. The blank determination is carried out exactly as is done in the case of the plant material, using as a starting point an empty platinum dish that is placed in the muffle along with the samples of plant material.

The amount of zinc on the standard curve corresponding to the per cent light transmission obtained for the unknown less the amount of zinc corresponding to the per cent transmission obtained for the reagent blank gives the amount of zinc present in the aliquot. From this the amount of zinc in the sample is easily calculated. As many as 12 determinations may conveniently be carried simultaneously through this procedure.

*Preparation of standard curve:* The data for the standard curve are obtained by determining the per cent transmission values for each of a series of solutions containing known amounts of zinc. These zinc solutions are prepared as follows:

Place 0, 5, 10, 15, 20, 25, 30, and 35 ml. of the standard zinc solution containing 10 micrograms of zinc per ml. in 100-ml. volumetric flasks. To each add one drop of methyl red indicator, N ammonium hydroxide until neutral, and 4 ml. of N hydrochloric acid, and make to volume. Proceed from this point in exactly the same manner as in the case of ash solutions, beginning with the first extraction and using 10-ml. aliquots of each of the zinc solutions. The 10-ml. aliquots contain 0, 5, 10, 15, 20, 25, 30, and 35 micrograms of zinc respectively.

The standard curve is constructed by plotting micrograms of zinc against per cent light transmission.

A saturated solution of dithizone in 0.01 N sodium hydroxide has a deep orange color similar to that of methyl-orange at a concentration of 1:1000. If 1 ml. of a freshly prepared reagent is diluted with 90 ml. of zinc-free water, and then shaken with a zinc solution of the same pH, a cherry-red color or precipitate is formed. Under suitable conditions, this color can be used for the determination of 0.001-1.0 mg. of zinc with an accuracy of 1 per cent.<sup>161</sup>

**Reagent.** Saturate 100 ml. of 0.01 N sodium hydroxide solution by shaking for 3 minutes with 0.5 g. of dithizone. Filter, and use the clear filtrate as the reagent. The solution usually becomes turbid after 1 or 2 days and should be used only as long as perfectly clear. One ml. of this solution is adequate for about 0.003 mg. of zinc.

**Standard zinc solution:** Dissolve 0.1000 g. of zinc in the least possible quantity of 1:4 sulfuric acid and dilute to 50 ml. Then make alkaline with 1 N sodium hydroxide to methyl-orange, used externally, and then dilute to 1 liter. This solution contains 0.1 mg. of zinc per ml. Dilute 2 ml. of this solution to 100 ml. to give a standard containing 0.002 mg. of zinc per ml.

**Procedure.** Make a preliminary determination of the zinc in order that the solution may be diluted so that in the final determination only 0.001-0.003 mg. of zinc per ml. is present. Also determine the alkalinity or the acidity of the sample by titrating an aliquot, and then neutralize with a suitable volume of 1 N sodium hydroxide or 1 N hydrochloric acid. Dilute until the concentration lies within the range mentioned. With the aid of a pipet transfer 1 drop of the reagent and 1 drop of the sample to a porcelain dish and observe the color. An immediate cherry-red precipitate appears if more than 0.01 mg. of zinc is present. The delayed appearance of a red color indicates 0.001-0.01 mg. of zinc per drop, and a pale red indicates less than 0.001 mg. of zinc per drop. If necessary, further dilute the sample so that 1 ml. contains 0.001-0.003 mg. of zinc.

To 98 ml. of water contained in a Nessler tube, add 1 ml. of the reagent and 1 ml. of the solution to be tested. Mix and compare with a standard solution similarly and simultaneously prepared. If the unknown contains less than 0.001 mg. of zinc per ml., dilute 1 ml. of the reagent to 50 ml., and add the zinc sample carefully and with mixing until the color corresponds to that of a standard containing 0.001, 0.002, or 0.003 mg. of zinc. From 0.001-1.0 mg. of zinc can be determined with an accuracy of about 7 per cent by this method.

**Titrimetric determination of zinc.** Several oxidizing agents destroy the red color of zinc dithizonate, probably by destroying some of the double bonds in the dithizone molecule. Hibbard <sup>46,47</sup> has used this principle as the basis for a titrimetric determination of zinc in plant and animal products. The titrating mixture is a solution of bromine in carbon tetrachloride.

**Reagents. Dithizone solution:** Dissolve 15 mg. of dithizone in 100 ml. of chloroform.

**Ammonium citrate solution:** Prepare a 10 per cent solution of citric acid and make alkaline with ammonium hydroxide. Then free from zinc by repeated extractions with dithizone in chloroform.

**Standard bromine solution:** Dissolve 1 ml. of pure bromine in 100 ml. of carbon tetrachloride as a stock solution. This should be preserved in a glass stoppered bottle and protected from light. To prepare the titrating solution, dissolve 1 ml. of the stock solution in 200 ml. of carbon tetrachloride and store in a dark bottle which is connected with a 2 ml. buret so that the buret may be filled automatically by suction applied at the top of the buret. The solution should be protected against contact with air or moisture. This solution gradually becomes weaker and must be checked each day or two.

Standardize the bromine solution as follows: Dissolve 7.4 mg. of arsenious oxide,  $\text{As}_2\text{O}_3$ , by heating with 0.2 g. of sodium bicarbonate, and dilute the resulting solution to 100 ml. One ml. of the arsenious oxide solution reduces the bromine solution closely equivalent to 5 $\gamma$  of zinc as the dithizonate. When freshly prepared, 1 ml. of bromine solution is equivalent to 7-9 $\gamma$  of zinc as the dithizonate.

The exact zinc equivalent of the bromine solution can be determined by titrating against known quantities of zinc, which have been separated with dithizone in the same manner as in the unknown.

**Procedure.** Place the solution in a conical separatory funnel having a volume approximately twice that of the solution to be analyzed. Make alkaline with dilute ammonium hydroxide, and if a precipitate forms, add hydrochloric acid until it is dissolved. Then add 1-2 ml. of ammonium citrate solution and again make alkaline with ammonia. The solution must remain clear with this treatment. Add several drops of dithizone solution and 5 ml. of chloroform. Shake vigorously for a few seconds and separate. The chloroform layer becomes red if zinc is present. Now add more reagent and again shake and repeat until the chloroform solution becomes purple or blue, indicating an excess of the reagent. The aqueous layer is yellow, also due to an excess of the reagent, unless considerable quantities of ammonium salts are present. When an excess of the reagent is present draw off the chloroform into a second separatory funnel and add more reagent and chloroform to the aqueous mixture and repeat the extraction. This should be repeated if the chloroform layer is not green or only slightly reddish. Combine this extract with the other chloroform solution in the second separatory funnel. This solution contains the zinc dithizonate. Remove the excess dithizone by shaking 2-3 times with 3 times its volume of 0.02 N ammonium hydroxide. Allow to settle each time, syphon off the aqueous layer and add more ammonium hydroxide. The washing may be regarded as complete when the aqueous layer is colorless and the chloroform layer is some shade of red.

Place the washed chloroform solution of zinc dithizonate in a 60-ml. narrow-mouth glass stoppered bottle, and add the bromine solution slowly and with frequent shaking until the red color fades to a colorless, or yellow solution. If the approximate quantity of bromine required is known, this may be added at

once. Allow the mixture to stand for several minutes to complete the reaction. The end-point with this titration is not distinct, and best results are obtained by adding an excess of bromine, allowing to stand for 5 minutes, then adding 1 ml. of 20 per cent potassium iodide solution, a little starch solution and 5 ml. of water containing 1 per cent sodium bicarbonate. Then titrate the iodine liberated with 0.001 N sodium thiosulfate solution.

Dithizone has been rather extensively used for the determination of zinc in plant materials; <sup>93,162,165-169,182</sup> foods; <sup>42,43,186</sup> and plant and animal products; <sup>47,92,161,186,196</sup> soil and soil extracts; <sup>46,186</sup> silicate rocks; <sup>26</sup> dust fumes; <sup>170</sup> aluminum alloys; <sup>188</sup> medicinal products; <sup>187</sup> commercial lead; <sup>171</sup> and babitt. <sup>172</sup>

**Detection and determination of cadmium.** Fischer and co-workers <sup>17,173</sup> observed that upon shaking a very dilute green solution of dithizone in chloroform or carbon disulfide with an aqueous neutral solution containing cadmium, a red color appeared. This reaction is sensitive to 0.01% of cadmium. Cadmium can be detected in the presence of zinc, lead, arsenic, antimony, tin, bismuth or iron by extracting from an alkaline tartrate solution. It can also be detected in the presence of silver or mercury by shaking out an alkaline solution to which hydroxylamine hydrochloride has been added. Copper interferes. Wolbling and Steiger <sup>183</sup> observed that when treating zinc and cadmium dithizonates with hydrogen sulfide, only the cadmium compound forms a sulfide. <sup>174,175</sup>

Fischer and Leopoldi <sup>176</sup> have used dithizone for determining small quantities of cadmium.

**Reagent.** Dissolve 50 mg. of dithizone in 1 liter of pure carbon tetrachloride.

**Procedure.** To 5-10 ml. of an approximately neutral solution containing 3-40% of cadmium, add an equal volume of 10 per cent sodium hydroxide solution. If ions are present which are precipitated by sodium hydroxide, add a little 20 per cent Rochelle salt solution. Use 5 ml. for 50 mg. of iron. Extract this mixture with successive portions of dithizone solution in a separatory funnel until the carbon tetrachloride solution is no longer red. Wash the extracted aqueous solution with a few ml. of carbon tetrachloride. Wash the combined extracts with 2 successive portions of 2 per cent sodium hydroxide having approximately one-half the volume of the carbon tetrachloride, and then wash once with a small volume of water. Transfer the carbon tetrachloride solution to a 25-ml. volumetric flask (or larger if necessary) and dilute to the mark with the same solvent. Transform the cadmium dithizonate to free dithizone by shaking the solution with 0.5 N hydrochloric acid. Compare with standards similarly prepared. If a photometer is used, determine the transmittancy at 620 m $\mu$ .

If only very small quantities of cadmium are present, the solution of cadmium dithizonate may be used for the comparison. The transmittancy is measured at 520 m $\mu$ .

The results obtained by this method agree within 5 per cent of the correct value.

Cadmium can be determined by the above method in the presence of all other ions except copper, silver, gold, mercury, palladium, nickel and cobalt.

The determination may be carried out directly in the presence of bismuth, lead, stannous tin, and moderate amounts of zinc by extracting with dithizone from an approximately 5 per cent sodium hydroxide solution. If zinc is present, a carbon tetrachloride solution of dithizone must be used.

Cadmium may be determined when silver or mercury is present if the cadmium is first converted into the complex pyridine thiocyanate, extracted with chloroform, and then, after destruction of the complex, treated with dithizone. The same procedure may be used with copper if the copper is first reduced to the cuprous state.

**Reagents.** *Dithizone solution:* Dissolve 50 mg. of dithizone in 1 liter of pure chloroform.

*Ammonium thiocyanate solution:* Dissolve 25 g. of ammonium thiocyanate in 100 ml. of water.

*Pyridine-chloroform mixture:* Mix 5 ml. of pyridine with 100 ml. of chloroform.

**Procedure.** To the slightly acid solution, add sufficient ammonium thiocyanate solution to redissolve any silver thiocyanate which first precipitated. If mercury is present, add 5 ml. of the ammonium thiocyanate solution for each 10 mg. of mercury. Add a 5 per cent sodium acetate solution until the pH is 5, or until blue Congo red paper just turns red. Extract the mixture with a number of small portions of the pyridine-chloroform mixture having a total volume of 15 ml. Wash the combined extracts once with an equal volume of 2 per cent ammonium thiocyanate solution.

Evaporate the chloroform extract to dryness on a water bath, add 3 ml. of concentrated nitric acid, and again evaporate to dryness. Dissolve the residue in 2-3 ml. of 1 per cent sulfuric acid, transfer to a separatory funnel, and rinse with a little water. Remove traces of silver and mercury by extracting with small portions of the dithizone solution. Dilute the aqueous solution to 10 ml. with water, and determine cadmium by the procedure described above.

If copper is present, add sodium carbonate to the solution until a turbidity appears, and then add a few drops of a 1 per cent sulfurous acid solution until the mixture is clear. Heat nearly to boiling, add 5-6 ml. of 1 per cent sulfurous acid for 30 mg. of copper, boil for a few moments, and then cool the mixture to room temperature. Adjust the acidity to pH 5 with sodium acetate as described above, and then add sufficient 25 per cent ammonium thiocyanate to redissolve any precipitated cuprous thiocyanate. Extract with the pyridine-chloroform mixture as described above. A little copper is extracted by the pyridine-chloroform mixture, and this must be removed by shaking with dithizone in acid solution before the cadmium determination.

Interference by zinc is eliminated by precipitating cadmium as the sulfide. Tin is removed by fuming with a mixture of bromine and hydrogen bromide, which causes the formation of volatile stannic bromide,



Dithizone may be used for the separation of cadmium from various metals. Cadmium dithizonate is extracted quantitatively from a faintly basic solution, but is readily decomposed by shaking the organic solvent solution with dilute acid. In this way cadmium can be separated from copper, mercury, silver, and other metals whose dithizonates are scarcely affected by dilute mineral acid solutions. Cadmium and cobalt are separated satisfactorily by this method, but nickel dithizonate is partially decomposed by dilute acids. The stability of cadmium dithizonate in strongly basic solutions is used for the separation of cadmium from bismuth, lead and zinc. Cadmium is extracted with a solution of dithizone in carbon tetrachloride from an aqueous solution which is 1 N in sodium hydroxide. Bismuth, lead and zinc are scarcely extracted at all under these conditions, even if present in relatively large quantity. Large amounts of zinc may, however, cause low results. Other metals extracted under the same conditions are copper, cobalt, mercury, nickel and silver.

Sandell<sup>177</sup> has used dithizone for the determination of cadmium in silicate rocks. The heavy metals contained in the sample are isolated by shaking the ammoniacal citrate solution, prepared from the decomposition products of the rock, with a carbon tetrachloride solution of dithizone. The carbon tetrachloride phase is separated and shaken with 0.01 N hydrochloric acid which decomposes the dithizonates of zinc, lead and cadmium, and these pass into the aqueous phase as chlorides. Copper and cobalt remain in the carbon tetrachloride solution. Cadmium is then extracted and determined by the following procedure:

**Reagents.** *Dithizone solution A:* A 0.02 per cent (w/v) solution of dithizone in carbon tetrachloride.

*Dithizone solution B:* A 0.001 per cent (w/v) solution of dithizone in carbon tetrachloride. One ml. of this solution when shaken with 10 ml. of redistilled water and 2-3 ml. of 25 per cent sodium hydroxide should yield a colorless carbon tetrachloride layer. This reagent should be prepared shortly before use by diluting dithizone solution A.

*Sodium citrate solution:* Prepare a 10 per cent solution of sodium citrate, and free from heavy metals by adding a few drops of ammonium hydroxide to 100 ml. of the solution and extracting with successive small portions of dithizone solution A until the latter shows only a faint pink color.

*Sodium hydroxide solution:* Dissolve 25 g. of sodium hydroxide in sufficient water to make 100 ml. of solution.

*Hydrochloric acid solution:* Dilute 1 volume of concentrated hydrochloric acid with 1000 volumes of redistilled water. Extract with 0.01 per cent dithizone solution in carbon tetrachloride before use.

**Procedure.** To 0.5 g. of the powdered sample contained in a platinum dish, add a few ml. of water, 1 ml. of 70 per cent perchloric acid and 5 ml. of hydrogen fluoride. Evaporate to dryness, add 0.5 ml. of perchloric acid and a few ml. of water and again evaporate to dryness. Now add 1 ml. of concentrated hydrochloric acid and 5 ml. of water and heat near boiling until all soluble matter has passed into solution. Add 10 ml. of the sodium citrate solution and

0.1 g. of hydroxylamine hydrochloride and neutralize with concentrated ammonium hydroxide to litmus, and then add 2 drops in excess. If the solution is turbid, filter and wash the residue with small portions of water. Ash the paper at low temperature and grind the residue in an agate mortar with 0.15-0.2 g. of sodium carbonate and fuse in a platinum crucible. Treat the melt with water, filter through paper, wash with a few ml. of water, and then rinse the insoluble material from the paper and heat with dilute hydrochloric acid to dissolve as completely as possible. Add 2-3 ml. of sodium citrate and a small crystal of hydroxylamine hydrochloride, neutralize with ammonium hydroxide and finally add 2 drops in excess.

*Extraction of main solution* (filtrate from insoluble materials): Add 5 ml. of dithizone solution A to the main filtrate in a separatory funnel and shake for 0.5-1.0 minutes. Allow to stand and draw off the carbon tetrachloride layer into a second separatory funnel. If the color of this layer is not green, add an additional 2-3 ml. of the reagent and again shake. Draw off the carbon tetrachloride and repeat the extraction until a greenish color appears in the carbon tetrachloride layer after shaking 1 minute.

*Extraction of solution from sodium carbonate fusion*: Extract the solution from the sodium carbonate fusion of the insoluble material in a manner similar to that described above except that 1 ml. portions of the reagent are used.

*Colorimetric determination*: Combine all dithizone extracts and shake with 5 ml. of water. Separate and discard the aqueous layer. Shake the carbon tetrachloride extract vigorously for 5 minutes with 5 ml. of 0.01 N hydrochloric acid. Separate the liquids and again shake the carbon tetrachloride layer with a fresh 5-ml. portion of 0.01 N hydrochloric acid. Combine the acid extracts and discard the carbon tetrachloride layer. Shake the acid extract with small portions of carbon tetrachloride and then separate as completely as possible all carbon tetrachloride from the aqueous layer.

Transfer the aqueous solution to a flat bottom glass stoppered tube ( $1.8 \times 15$  cm.) and rinse the separatory funnel with 1-2 ml. of water. Prepare a series of standards containing 0.05, 0.1, 0.15, etc.  $\gamma$  of cadmium. Dilute the standard with 0.01 N hydrochloric acid until the volume is the same as that of the unknown and mix well. Add 2.5 ml. of 25 per cent sodium hydroxide to each and again mix. Then add 1.0 ml. of dithizone solution B and shake vigorously 10-15 times. Compare the colors of the carbon tetrachloride layers by viewing tubes transversely against a white background. The colors fade on standing. The tubes containing the standards and unknown should be similar. A blank should be run on the reagents used, using quantities double those employed in the determination.

**Determination of bismuth.** Bismuth reacts with dithizone to form an orange-yellow dithizonate which is soluble in chloroform and carbon tetrachloride. This reaction has frequently been used for the separation of bismuth as a preliminary to its actual determination by the iodide or other methods, and also for the colorimetric determination of the metal. According to Hubbard<sup>211</sup> and Reith and van Dijk,<sup>178</sup> bismuth is only incompletely extracted from basic

citrate solutions containing high concentrations of salts, although Haddock<sup>89</sup> reports that the extraction of bismuth is complete in the presence of citrate and also cyanide. The extraction is less complete in strongly alkaline solutions. Fischer<sup>10</sup> recommends a pH of 7-8 for the extraction with a solution of dithizone in carbon tetrachloride. In a procedure described by Hubbard,<sup>211</sup> the pH for the extraction is adjusted to 9.5, while Sandell<sup>204</sup> uses a slightly lower value of 8.5-9.0.

Bismuth can be separated from cadmium, copper, silver and zinc by carrying out the extraction in the presence of cyanide. Lead, stannous tin and thallium also react with dithizone in an alkaline cyanide solution. Bismuth may be separated from lead and thallium if the latter are present in not too great a quantity by making use of the fact that bismuth dithizonate is comparatively stable in dilute mineral acid solutions. When the acidity of an aqueous solution containing bismuth and lead is adjusted to pH 3, and is then shaken with several successive portions of a carbon tetrachloride solution of dithizone, the bismuth is completely transferred to the organic solvent, while practically all lead remains in the aqueous layer.<sup>75</sup> An appreciable quantity of lead is extracted at pH 4.

When less than 10% of bismuth is to be determined, the dithizone method is recommended, and fairly accurate results are obtained with as little as 1% of the metal. The following method, which is described by Sandell,<sup>204</sup> is essentially the same as that reported by Hubbard:<sup>211</sup>

**Reagents.** *Dithizone solution:* Dissolve 25 mg. of dithizone in 1 liter of pure chloroform. Store in a cold, dark place.

*Ammonia-cyanide solution:* Add 20 g. of potassium cyanide to 150 ml. of concentrated ammonium hydroxide, and dilute with water to 1 liter. If necessary, purify the potassium cyanide by extracting a 50 per cent solution with dithizone in chloroform, and then with pure chloroform to remove the excess dithizone.

*Standard bismuth solution:* Prepare a 0.0010 per cent solution of bismuth in 1:100 nitric acid by dissolving the metal in nitric acid and diluting to the proper concentration.

**Procedure.** *Isolation of bismuth:* Use a sample of biological material of such size that the aliquot used for the final determination will contain 5% or more of bismuth. Destroy the organic matter by wet oxidation with sulfuric and nitric acids, and adjust the acidity of the diluted digestion mixture to 0.2-0.3 N with a 4 N sodium hydroxide solution. Add to the solution, which should have a volume of 50-100 ml., 1 mg. of copper to form copper sulfide and treat with hydrogen sulfide for one-half hour. Allow the reaction mixture to stand overnight, and filter off the precipitate through a small dense filter paper. Wash once or twice with 5 ml. of 0.1 N hydrochloric acid saturated with hydrogen sulfide. Transfer the filter and precipitate to the vessel in which the precipitation was carried out, add 10 ml. of 1:3 nitric acid, and heat gently to dissolve the sulfides. Filter through a fine, sintered-glass filter crucible, and wash with hot dilute nitric acid. Evaporate the filtrate to a small volume to remove most of the nitric acid.

*Extraction of bismuth, thallium and lead:* Transfer the nitric acid solution, or a suitable aliquot of it, to a 125-ml. Pyrex separatory funnel. Dilute to approximately 50 ml., add a few drops of thymol blue solution, and 5 ml. of 10 per cent potassium cyanide solution. Adjust the pH of the solution to 8.5-9.0 with ammonia, and shake with several successive 5-ml. portions of the dithizone solution. Bismuth dithizonate, which is orange in color, passes into the chloroform layer. Continue the extraction until the final portion of dithizone shows no color change after shaking for 1 minute. Wash the aqueous solution with 2-3 ml. of chloroform, and add the washings to the chloroform extracts. Add 2 ml. of concentrated nitric acid to the aqueous phase, and adjust the pH of the solution to 8.5-9.0 with 1:9 ammonia. Extract with two 5-ml. portions of dithizone solution.

Shake the combined chloroform extracts with 25 ml. of water, and draw off the chloroform solution into a second separatory funnel. Shake the aqueous layer with a few ml. of the dithizone solution, and add the latter to the other extracts. Now extract the bismuth from the chloroform solution by shaking with an aqueous acid solution. If not more than 50 $\gamma$  of bismuth is present, use the entire chloroform solution, but with a greater quantity of the metal, use a suitable aliquot. The quantity of bismuth in the sample is determined approximately by the amount of dithizone required for the extraction, since 5 ml. of the dithizone solution extracts 25 $\gamma$  of bismuth. Shake the chloroform solution (or aliquot) thoroughly with two 25-ml. portions of 1:100 nitric acid and discard the chloroform layer. Shake the aqueous solution with 1-2 ml. of chloroform to remove droplets of the chloroform-dithizone solution.

*Separation of bismuth from thallium and lead:* Add 2-3 drops of *m*-cresol purple or thymol blue to the acid extract, and adjust the pH to 2.5-3.0 with 1:9 ammonia. Shake thoroughly with a number of 5-ml. portions of dithizone solution, and combine the chloroform extracts in a second separatory funnel. Transfer the bismuth to the aqueous phase by shaking the chloroform solution with two 25-ml. portions of 1:100 nitric acid. Draw off the chloroform as completely as possible from the bottom of the funnel, and then allow the latter to stand for some time unstoppered to allow any chloroform to evaporate from the surface of the solution.

*Determination of bismuth:* To 50 ml. of the acid solution, add 10 ml. of the ammonia-cyanide mixture, and then add a dithizone solution whose volume and concentration are determined by the approximate amount of bismuth present as determined in the previous extraction. This is shown in Table 105.

Shake the mixture for 15 seconds, separate the chloroform layer, and free from droplets of water, and then transfer to a suitable cell as indicated in the above table. Determine the optical density of the chloroform solution, using light of wave length 505  $m\mu$ . Determine bismuth by reference to a standard curve prepared from known quantities of bismuth in 1:100 nitric acid solution saturated with chloroform.

Bismuth may also be determined by a series of standards method. When this procedure is used, from 1 to 3 $\gamma$  of bismuth in 5 ml. of 1:100 nitric acid is

suitable. Shake with about 2 ml. of 0.001 per cent dithizone solution after adding 1 ml. of ammonia-cyanide solutions. Compare with standards in the usual manner.

TABLE 105.

Amount of Bismuth $\gamma$	Dithizone Concentration mg./liter	Volume of Dithizone ml.	Cell Length mm.
0-5	6	10	50
0-25	12	25	25
0-50	25	25	12

Haddock<sup>39</sup> has used dithizone for the extraction of bismuth as a preliminary to the colorimetric determination of bismuth by the iodide method. This method is suitable for determining 0.005-0.1 mg. of bismuth. Not more than 0.5 mg. of lead or thallium should be present.

**Procedure.** To determine bismuth in plants or animal materials, destroy the organic matter by wet oxidation, using concentrated sulfuric acid and 30 per cent hydrogen peroxide. In analyzing metals or alloys dissolve in acid and remove the excess acid by evaporation. Simply dissolve metallic salts in water. To the neutral or acid solution contained in a separatory funnel, add 2 g. of citric acid (10 g. if large quantities of iron are present) and neutralize to litmus with concentrated ammonia while cooling with running water. Now add 10 ml. of approximately 10 per cent ammonia, or a sufficient quantity to make the reaction mixture alkaline, and then 2 g. of potassium cyanide (5-10 g. of potassium cyanide if large quantities of copper or silver are present). Extract the cold solution by shaking vigorously with four 15-ml. portions of 0.1 per cent dithizone in chloroform. Wash each extract with 10 ml. of water contained in a second separatory funnel and then transfer the extract to a 100-ml. Kjeldahl flask. Remove the chloroform by evaporation and add 1 ml. of concentrated sulfuric acid. Heat carefully over a microburner while adding dropwise 30 per cent hydrogen peroxide until all organic matter is destroyed. Transfer the acid solution to a separatory funnel with 20 ml. of water which has been well cooled. Destroy any excess sulfur dioxide by adding dropwise a little very dilute iodine solution. Add 4 drops of approximately 5 per cent sulfurous acid solution, 2 ml. of 30 per cent hypophosphorus acid and 5 ml. of freshly prepared 10 per cent potassium iodide solution. Extract the mixture by shaking with successive 3-ml. portions of a mixture of 3 parts of amyl alcohol and 1 part of ethyl acetate until the final extract is almost colorless. Collect the extracts in a small graduated cylinder. Prepare a standard by adding a known quantity of 0.001 per cent bismuth solution to the aqueous solution and extracting as before. Several standards may be prepared. Each of a series of extracts is adjusted to the same volume (about 6 ml. for 10-40 $\gamma$  of bismuth and 10-12 ml. for 40-100 $\gamma$ ). Filter through cotton and compare the color of the unknown with that of the standards.

From 0.0002-0.005 per cent of bismuth in commercial copper can be determined by extracting from an ammoniacal potassium cyanide solution with a chloroform solution of dithizone. The chloroform is removed by evaporation, and the lead is precipitated as the sulfate. Bismuth is then determined colorimetrically by the iodide method: <sup>40,41,212</sup>

**Procedure.** Dissolve 2 g. of the drillings in 50 ml. of nitric acid and evaporate to fumes with sulfuric acid. Cool, dissolve in water, and add 1 g. of citric acid dissolved in 20 ml. of water. Add sufficient ammonium hydroxide to make alkaline and dissolve the copper salts. Cool and add 50 ml. of a freshly prepared 20 per cent potassium cyanide solution. Transfer to a 250-ml. separatory funnel and dilute to 200 ml. with water. Extract the bismuth by shaking with a number of 10-ml. portions of a 0.1 per cent solution of dithizone in chloroform. Draw off the chloroform extracts into a 150-ml. separatory funnel, and treat the aqueous layer with additional 10-ml. portions of the reagent until extraction is complete. Withdraw almost all the third extract and shake the aqueous layer with 5 ml. of chloroform. Combine the chloroform layer with the other extracts and wash with 50 ml. of distilled water.

Remove the chloroform by evaporation, and mix the residue with 1 ml. of sulfuric acid. Heat to the strong evolution of sulfur trioxide, cool slightly, and cautiously add 2-3 ml. of 20 volume per cent hydrogen peroxide and continue the evaporation until fumes are evolved and the liquid is colorless. Cool, dilute with 150 ml. of water, filter off any lead sulfate, and determine the bismuth colorimetrically as described above.

Reith and van Dijk <sup>178</sup> report that from 2-200 $\gamma$  of bismuth can be titrated quantitatively with dithizone at a pH of 4.0 in the absence of citrates, cyanides and phosphates. The presence of lead in concentrations similar to that of bismuth presents no difficulty. Larger quantities of lead must be removed prior to the titration. <sup>108</sup>

Yu-Lin Yao <sup>109</sup> has proposed a titrimetric method for the determination of traces of bismuth in copper by means of dithizone. Bismuth is first collected by hydrated manganese dioxide, and then bismuth and lead are extracted in an alkaline cyanide medium by a solution of dithizone in carbon tetrachloride. Bismuth is finally titrated with a standard dithizone solution at pH 3.

Kammerman <sup>106</sup> has used dithizone for the estimation of bismuth and other metals in a systematic scheme for the analysis of viscera for poisons.

**Determination of thallium.** Thallous thallium is extracted quantitatively from an alkaline cyanide solution of pH 9-12. According to Fischer, the optimum pH is 11 when a carbon tetrachloride solution of dithizone is used. Thallium can be separated from most metals in this way, but lead, bismuth and stannous tin accompany thallium in the extraction. Manganese also tends to accompany thallium, and a second extraction should be made following the destruction of dithizone in the first extract if much manganese is present. Haddock <sup>179</sup> reports that relatively large quantities of zinc, mercury and nickel cause the extraction of thallium to be incomplete.

The following method is used for the isolation of thallium as a preliminary to the actual determination by some other method.

**Procedure.** Reduce thallium to the thallous state with hydroxylamine hydrochloride or sulfurous acid. To approximately 50 ml. of the nearly neutral sample solution, add 0.5 g. of potassium cyanide and 0.5 g. of ammonium citrate. Extract the mixture with four 10-15 ml. portions of 0.1 per cent dithizone in chloroform. Combine the extracts and wash with 20-50 ml. of 1:1000 ammonia. Separate the chloroform layer and shake the aqueous phase with a few ml. of dithizone solution to recover any thallium that may have passed into the ammonia solution. Evaporate the chloroform extracts to dryness in a small Erlenmeyer flask and allow to cool. Add to the residue 1 ml. of concentrated sulfuric acid and heat, and then add 30 per cent hydrogen peroxide in small portions until all organic matter is destroyed. Use the resulting solution for the determination of thallium.

Bambach<sup>120</sup> has determined small quantities of thallium in pharmaceutical chemicals by a mixed-color method previously described for lead.

Kamerman<sup>196,197</sup> has used the following titrimetric method for the toxicological examination of viscera for thallium:

**Procedure.** Digest the viscera with sulfuric and nitric acids in a Kjeldahl flask to destroy organic matter and allow the mixture to cool. Dilute to a definite volume, mix well, and use a suitable aliquot for the determination. Add about 30 per cent of citric acid and then make slightly alkaline with ammonium hydroxide. Add a little 10 per cent potassium cyanide solution and 5 ml. of 5 per cent hydroxylamine hydrochloride solution. Extract the mixture with several successive portions of a 0.05 per cent dithizone solution in chloroform until the last portion shows no change in color. Shake the combined chloroform extracts with a buffer of pH 3-4 until all lead, thallium and traces of tin are transferred to the aqueous layer. If tin is present, shake with dithizone solution until it is removed. Make the aqueous solution containing the lead and thallium alkaline (pH 9), and again extract with the dithizone solution. Separate the chloroform extract, and evaporate to dryness, and then destroy all organic matter by boiling with sulfuric acid, which leaves lead and thallium as the sulfates. Cool the acid solution, and carefully dilute with water. Add ethyl alcohol and filter off the precipitate of lead sulfate. Evaporate the filtrate until all alcohol is removed, and adjust the pH to 9 by the addition of dilute ammonium hydroxide. Titrate the solution with small quantities of 0.005 per cent dithizone solution which has been standardized against known quantities of thallium.

The recovery of thallium by this method is said to be 96-100 per cent complete.

**Detection of bromine.** When a solution prepared by dissolving 0.3 mg. of dithizone in 100 ml. of carbon tetrachloride is added dropwise to anhydrous carbon tetrachloride containing a trace of bromine, a yellow to pale red color first appears, and on further addition of the reagent this changes to an intense

red with a tinge of blue-violet. This reaction constitutes an extraordinarily sensitive test for bromine.<sup>190</sup> To detect bromides, add to the solution to be tested a little dilute sulfuric acid and hydrogen peroxide, and then extract the bromine formed with carbon tetrachloride. Filter twice through paper, and then test for bromine as described above.

Chloride does not interfere. In the presence of iodide, add sulfuric acid and then solid sodium nitrite. Heat to expel iodine and the oxides of nitrogen, shake with carbon tetrachloride, draw off the aqueous solution, and warm with hydrogen peroxide and ammonium persulfate. Extract bromine with carbon tetrachloride and proceed as described above.

**Dithizone in spectral analysis.** A solution of the dithizone complexes of copper, silver, gold, zinc, cadmium, mercury, thallium, tin, lead, bismuth, manganese, cobalt, nickel and palladium in carbon tetrachloride can be used advantageously for producing spectra with the aid of electric sparks.<sup>181</sup>

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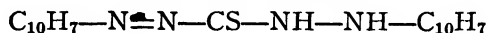
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### DI- $\beta$ -NAPHTHYLTHIOCARBAZONE

$C_{21}H_{16}N_4S$

Mol. Wt. 356.40



**Use** Determination of mercury and zinc.

The following method for the preparation of the reagent has been described by Hubbard and Scott.<sup>1</sup>

**Reagents.** *Sodium acetate solution:* Dissolve 40 g. of sodium acetate (tri-hydrate) in sufficient water to make 100 ml. of solution.

*Nitromethane solution:* Mix 4.8 ml. of the sodium hydroxide solution with 13.5 ml. of absolute alcohol and 1.6 ml. of nitromethane. Cool the mixture to  $-5^\circ C.$  and add 100 ml. of cold water. Shake until solution is complete, and again cool to  $-5^\circ C.$  Just before use, mix the solution with an additional 4.8-ml. portion of the sodium hydroxide solution and transfer to a separatory funnel containing a little cracked ice.

**Preparation.** *Nitroformazyl:* Mix 8.6 g. of  $\beta$ -naphthylamine with 15 ml. of concentrated hydrochloric acid in a 150-ml. beaker, and add with stirring 25 ml. of water. Cool to  $0^\circ C.$  and add 5 g. of sodium nitrite dissolved in 10 ml. of water. Filter and collect the filtrate in a 500-ml. round bottomed flask. Immerse the flask in a bath of salt and cracked ice, and when the mixture is cooled to  $-10^\circ C.$ , add dropwise and with constant stirring 40 ml. of the sodium acetate solution.

While keeping the temperature at  $-5^\circ C.$ , add slowly and with stirring from the separatory funnel the alkaline nitromethane solution. Nitroformazyl separates as a maroon-colored precipitate. Allow the mixture to stand for 30 minutes and filter with suction. Wash with water, transfer to a 150-ml. beaker and add 30 ml. of 50 per cent acetic acid. Warm gently with stirring until the temperature reaches  $40^\circ C.$ , and then cool to room temperature. Filter with suction and wash the precipitate with 50 ml. of 10 per cent acetic acid, and finally wash with water to remove the acid. Allow to dry in air and grind the dried product in a mortar. Treat with 150 ml. of absolute alcohol, and boil with

stirring. Filter, wash with 20 ml. of hot alcohol, and suck as dry as possible and dry in air.

*Di- $\beta$ -naphthylthiocarbazide*: Divide the nitroformazyl compound into 1-g. portions, and treat each portion as follows: Mix with 40 ml. of absolute alcohol in a large test tube, which is immersed in an ice bath. Pass ammonia gas through the mixture for about 15-25 minutes, and then pass hydrogen sulfide gas through the mixture with occasional stirring until the carbazide separates. The completion of the reaction is indicated by a change of color from maroon to yellow. At this point add 20 ml. of cold water with stirring and filter immediately through a Buchner funnel.

*Di- $\beta$ -naphthylthiocarbazon*e: Immediately treat the carbazide while still moist with 20 ml. of 5 per cent alcoholic potassium hydroxide at room temperature. Mix well and break up any lumps which form with the aid of a stirring rod. Immediately neutralize the clear red solution with 1 liter of a dilute solution of hydrochloric acid (4 ml. of 6 N hydrochloric acid per 100 ml.). Filter on a Buchner funnel and dry.

The impure product is divided into 1-g. portions and each is treated as follows: Dissolve in 100 ml. of redistilled chloroform which has been distilled from pyrex glass and treated with hydroxylamine. Heat gently until solution is complete, and then wash the chloroform solution with three 25-ml. portions of distilled water. After each washing the chloroform solution should be removed to a clean separatory funnel. Filter the washed chloroform solution through fluted paper into a glass evaporating dish and evaporate to 10 ml. Allow to cool to room temperature and add 50 ml. of absolute alcohol. Filter on a small paper in a Buchner funnel and wash once with 10 ml. of absolute alcohol, using suction. Evaporate all of the alcohol.<sup>1,2,3</sup>

**Determination of mercury.** The reactions of di- $\beta$ -naphthylthiocarbazon with salts of the heavy metals have been studied by Suprunovich,<sup>2</sup> who has reported that the reagent is very similar to dithizone in its behavior, but that it is characterized by a greater sensitivity of reaction. Since the mercury complex of di- $\beta$ -naphthylthiocarbazon is red, a color particularly suited for "mixed-color" technique, Hubbard<sup>4</sup> has studied the properties of the complex to determine its suitability for the determination of mercury in biological materials.

The procedure developed for the determination of mercury in urine consists of oxidizing the organic matter of the samples with potassium permanganate in the presence of sulfuric acid, and then extracting mercury in two steps: the first extraction is to remove copper, which is the only interfering element found in urine; and the second is to separate mercury as the pure complex of di- $\beta$ -naphthylthiocarbazon for the final photometric estimation. The method is said to be very sensitive, and an accuracy of  $\pm 0.2\gamma$  is claimed for  $5\gamma$  or less of mercury. For quantities of mercury exceeding  $50\gamma$  the error does not exceed  $\pm 2$  per cent. In general, this reagent is used in a manner similar to dithizone.

**Determination of zinc.** Cholak and co-workers<sup>5</sup> have used di- $\beta$ -naphthylthiocarbazon in place of dithizone for the extraction of zinc from solutions

of ashed biological materials as a preliminary to the determination of zinc. The substitution of di- $\beta$ -naphthylthiocarbazone offers a number of advantages. These are (a) the elimination of partition losses which occur with dithizone over the pH range 8.3-10.5; (b) the elimination of loss of zinc which occurs when sodium diethyldithiocarbamate is used to prevent interference by other ions in the extraction; and (c) this substitution has made possible the derivation of standardization curves which agree with Beer's law over their entire range; and (d) also makes possible the addition of sodium diethyldithiocarbamate to the zinc solution before the initial extraction. This permits the fixation of the range and the extraction of zinc in sufficient purity to be determined either colorimetrically or polarographically.

If 0.2 N hydrochloric acid is substituted for 0.02 N acid, at least 60% of zinc may be recovered from the di- $\beta$ -naphthylthiocarbazone-carbamate-chloroform solution with a single 50-ml. portion of acid, while eliminating interference by copper, cobalt, nickel, mercury and silver.

Best results are obtained when very small quantities of zinc are estimated colorimetrically if the sample contains no cadmium. If cadmium is present, or if the zinc concentration exceeds 0.05 mg. per 10 ml. of solution, the polarographic method is recommended.

The method used is similar in its general outline to the dithizone method.

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## CHAPTER XIX

### MISCELLANEOUS IMINO COMPOUNDS

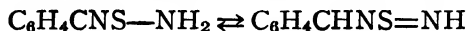
#### 2-AMINOENZOTHIAZOLE

Synonym: Benzthiazolonimide

$C_7H_6N_2S$

Mol. Wt. 150.18

Beil. Ref. XXVII, 365, 182



**Use:** Detection of mercury and silver.

2-Aminobenzothiazole is obtained as leaves from water. It melts at 122-125° C. It dissolves in alcohol, ether, and chloroform, but it is difficultly soluble in water. It also dissolves in concentrated acids.

**Preparation:** Mix 10 ml. of benzothiazole, 7 g. of hydroxylamine hydrochloride and 100 ml. of 2 N sodium hydroxide, and boil for 2 hours under reflux. Collect the crystals which separate on cooling, and purify by recrystallizing from benzene to which has been added a little decolorizing charcoal. The product may be recrystallized from water.<sup>1,2</sup>

2-Aminobenzothiazole is also prepared by heating 1-phenylthiosemicarbazide with 20 per cent hydrochloric acid in a tube at 125-130° for 12 hours.<sup>2</sup>

**Reaction with silver.** 2-Aminobenzothiazole reacts with a neutral solution of silver nitrate to give a crystalline precipitate of  $AgC_7H_5N_2S$ . If this precipitate is dissolved in concentrated ammonium hydroxide and warmed on a water bath, yellow  $Ag_2C_7H_4N_2S$  is precipitated. As little as 0.04 mg. of silver in 2 ml. may be detected.

**Reaction with mercury.** An aqueous solution of mercuric nitrate when treated with a large excess of 2-aminobenzothiazole in the presence of sodium acetate, and heated 1 hour on a water bath, gives a deep yellow precipitate of  $HgC_7H_4N_2S$ .<sup>3</sup> The reagent also reacts with mercuric chloride in ethyl alcohol to give an addition compound. This compound turns a pure yellow when heated with water.

Aqueous mercuric chloride reacts with the reagent in the presence of sodium acetate when warmed on a water bath, and yields a precipitate of  $Hg_2ONO_8C_7H_5N_2S$ .

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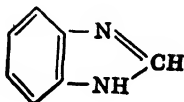
#### BENZIMIDAZOLE

$C_7H_6N_2$

Mol. Wt. 118.13

Beil. Ref. XXIII, 131.





**Use:** Detection of cobalt.

Benzimidazole is a crystalline solid melting at 170° C. It is slightly soluble in cold water, but dissolves more readily in hot water. It is quite soluble in alcohol, but only slightly soluble in ether and is almost insoluble in benzene.

**Preparation:** Place 54 g. of *o*-phenylenediamine in a 500-ml. round-bottom flask and add 32 ml. of 90 per cent formic acid. Heat the mixture in a boiling water bath for 2 hours and allow to cool. When cool, add 10 per cent sodium hydroxide slowly and with thorough mixing until the mixture is just alkaline to litmus. Filter with suction, using ice water for transferring the material to the filter. Press out as much of the liquid as possible on the filter, and then wash with 50 ml. of cold water.

Dissolve the crude product in 750 ml. of boiling water, and digest the mixture for 15 minutes with 2 g. of decolorizing charcoal. Filter rapidly through a heated filter and cool to 10-15°. Filter the purified crystals and wash with 50 ml. of cold water. Dry at 100°. <sup>1,2</sup>

**Detection of cobalt.** A violet-blue crystalline precipitate is obtained when an alcoholic solution of benzimidazole is added to an ammoniacal solution of a cobalt salt. Under similar conditions the nickel salt is not precipitated immediately, but upon long standing a gray-violet precipitate forms. In the presence of nickel, however, a nickel-free cobalt precipitate cannot be obtained even by repeated precipitation. Even if all cobalt is precipitated from a pure cobalt solution by means of benzimidazole, a further precipitation takes place upon the addition of a nickel salt. By making use of this fact, the sensitivity of the cobalt test with benzimidazole can be materially increased. In a pure solution, 0.0794 mg. of cobalt in 5 ml. of solution can be detected, but in the presence of 0.1 g. of nickel the sensitivity of this reaction is increased to 0.006 mg. of cobalt in 5 ml. By means of this reaction traces of cobalt can be detected in nickel salts. <sup>3</sup>

**Procedure.** Dissolve 1 g. of the nickel salt to be analyzed in 5 ml. of water, and add a few drops of ammonium chloride solution and concentrated ammonium hydroxide, and then add a little alcoholic solution of benzimidazole. As little as 0.006 per cent of cobalt can be detected by this reaction.

Yagoda <sup>4</sup> has used this reaction as the basis for a semi-quantitative method for determining cobalt by a spot test. By restricting the area in which the reaction may occur by means of a water repellent substance, the quantity of cobalt present can be approximately established by the color of the test paper. A 5 per cent solution of the reagent in methyl alcohol is used.

**Formation of salts with benzimidazole.** Feigl and Gleich <sup>5</sup> have investigated the formation of salts with benzimidazole. These salts are given in Table 106.

TABLE 106.

Cation	Formula of Salt
Mercury .....	$C_7H_5N_2HgCl$
Copper .....	$4C_{14}H_{10}N_4Cu \cdot NH_3 \cdot H_2O$
Cadmium .....	$C_{14}H_{10}N_4Cd$
Cobalt .....	$C_{14}H_{10}N_4Co$
Zinc .....	$C_{14}H_{10}N_4Zn$
Zinc .....	$4C_{14}H_{10}N_4Zn \cdot NH_3 \cdot H_2O$

The mercury salt is precipitated with an alcoholic solution of benzimidazole in the presence of sodium acetate. The copper salt is precipitated from an ammoniacal copper salt solution, and cobalt is precipitated from an ammoniacal solution in the presence of ammonium chloride.

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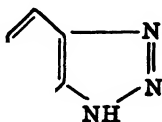
## BENZOTRIAZOLE

Synonym: 1,2,3-Benzotriazole

$C_6H_5N_3$

Mol. Wt. 119.10

Beil. Ref. XXVI, 38.



**Use:** Determination of copper, silver, and zinc.

Benzotriazole is obtained as needle-like crystals from chloroform. It melts at 96-97° C.

**Preparation:** Place 108 g. of *o*-phenylenediamine, 115 ml. of glacial acetic acid and 300 ml. of water in a 1-liter beaker, and warm slightly to obtain a clear solution. Cool to 5° C. by immersing in ice water, and then add, all at once, with stirring, a cold solution of 75 g. of sodium nitrite in 120 ml. of water. The color turns to a dark green, and the temperature rises to 70-80° C., and then the solution turns a clear orange-red. Remove the beaker from the cooling bath, and allow the mixture to stand for 1 hour. The benzotriazole separates as an oil. Pack the beaker in ice, and stir until the contents solidify. Keep the mixture cold for 3 hours, and collect the precipitate on a Buchner funnel. Wash with 200 ml. of ice water. Suck as dry as possible, and then dry at 45-50° C. overnight. Place in a 200-ml. modified Claisen flask, and distill under reduced pressure. Collect the fraction boiling at 201-4° C. at 15 mm. or 156-9° C. at 2 mm. Melt the product in the receiver over a luminous flame, and pour into

250 ml. of benzene. Stir the solution until crystals begin to separate, then chill the mixture for 2 hours, and collect the product on a Buchner funnel.<sup>1,2</sup>

**Determination and separation of copper.** 1,2,3-Benzotriazole forms a precipitate of  $\text{Cu}(\text{C}_6\text{H}_4\text{N}_3)_2$  with cupric ions. Precipitation is carried out in a solution containing tartaric and acetic acids at a pH of 7.0-8.5. A 2 per cent aqueous solution of the reagent is used as the precipitant. The precipitate contains 21.24 per cent copper, and can be weighed directly, but best results are obtained by igniting to cupric oxide and determining the copper in a nitric acid solution iodometrically. As little as 0.2 mg. of copper gives a titratable precipitate.<sup>3</sup> Ferrous, silver, nickel, cadmium, zinc and cobalt ions give similar precipitates, but ferric, arsenic, tin, antimony, chromium, aluminum, molybdenum, selenium and tellurium do not interfere. The use of benzotriazole as a reagent for copper is to be recommended, since it makes possible a clean separation from hexavalent molybdenum, tetravalent selenium and tellurium, pentavalent antimony, and pentavalent arsenic, which may interfere in the usual iodometric titration.

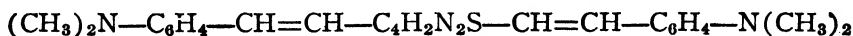
Remington and Moyer<sup>4</sup> have conducted a qualitative study of the reagent, and have reported gravimetric procedures for the determination of copper, silver and zinc.

1. L. F. Fieser and E. L. Martin, *J. Am. Chem. Soc.* **57**, 1835 (1935).
2. R. E. Damschroder and W. D. Peterson, *Organic Synthesis*, **20**, 16.
3. J. A. Curtis, *Ind. Eng. Chem., Anal. Ed.* **13**, 349-51 (1941); *C.A.* **35**, 4306 (1941).
4. W. J. Remington and H. V. Moyer, *Dissertation Abst.* No. 24, Columbus, Ohio, Ohio State Univ. Press (1937).

## BIS-DIMETHYLAMINOSTYRYLTHIOPYRIMIDONE

$\text{C}_{24}\text{H}_{25}\text{N}_4\text{S}$

Mol. Wt. 401.50



**Use:** Detection of silver, mercury, gold and palladium.

**Preparation:** Dissolve 1.2 g. of dimethylthiopyrimidone with 2 g. of *p*-dimethylaminobenzaldehyde in 10 ml. of pyridine and add 5 drops of piperidine, and then reflux for 5 hours. Precipitate the reagent with water, and purify the impure base twice with boiling 1 N sulfuric acid.

The reagent is prepared by dissolving 0.05 g. of the sulfate obtained above with a drop of dilute sulfuric acid in 100 ml. of methyl alcohol. Filter and saturate filter paper (Schleicher and Schull No. 598), dry, and store in a dark place.

**Detection of metals.** The reagent, which is readily separated in the form of a difficultly soluble sulfate, dissolves in alcohol with the formation of a deep blue colored solution. The addition of acid up to 0.1 N does not change this color, although the color changes to green with the addition of more acid. Alkalies change the color from blue to reddish-brown. The addition of a salt of mercury, silver, gold or palladium to the blue, weakly acid solution of the dye

produces a reddish-brown color. This color is formed with mercury salts even in the presence of chloride ions. The test for the above metals is most satisfactorily carried out by applying the drops of the solutions to be tested to the reagent paper prepared as described above. In this way the identification of 0.01% of mercury in a 0.1 N hydrochloric acid solution is not disturbed by the presence of 1 per cent solutions of salts of cadmium, arsenic, tin, nickel, cobalt, iron, chromium, aluminum, manganese and zinc.

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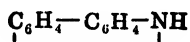
## CARBAZOLE

Synonym: Diphenyleneimine, dibenzopyrrole

$C_{12}H_9N$

Mol. Wt. 167.20

Beil Ref. XX, 433.



**Use:** Detection of nitrate and nitrite.

Determination of nitrate.

Carbazole is a white crystalline solid. It melts at 243° C. and boils at 352-354° C. It is insoluble in water, slightly soluble in alcohol and toluene, and soluble in benzene, chloroform, acetic acid, ether, carbon disulfide and carbon tetrachloride.

**Detection and determination of nitrate.** Graebe and Glaser<sup>1</sup> discovered that small quantities of oxidizing agents produce a dark green color when added to a solution of carbazole in concentrated sulfuric acid. This reaction has been used for the detection and colorimetric determination of small quantities of nitrate,<sup>2-8</sup> although the method is less satisfactory than others which have been proposed. The following method may be used for the determination of nitrate in water.

**Procedure.** Mix a measured quantity of the water to be analyzed (2 ml. or less) with 4 ml. of concentrated sulfuric acid. Cool, and add a small quantity of sulfuric acid containing a little carbazole. Compare the resulting mixture with a second solution similarly prepared, and containing a known quantity of nitrate. The sensitivity of this reaction is 2 p.p.m. of nitrate.

**Detection of nitrite.** Fearon<sup>9</sup> has used the following method for detecting nitrite in urine:

**Procedure.** To a few ml. of concentrated sulfuric acid in a test tube, add a very small quantity of the reagent and shake. No color change occurs if the sulfuric acid is pure. Next add a drop of the urine to be tested. If nitrites are present, a deep green color develops.

The sensitivity of this reaction is 1:500,000.

1. C. Graebe and C. Glaser, *Ann.* 163, 347 (1872).
2. S. C. Hooker, *Am. Chem. J.* 11, 249 (1889).

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9. W. A. Fearon, *J. Am. Med. Assn.* **74**, 1128 (1919).

## DICYANDIAMIDE



Mol. Wt. 84.05

Beil. Ref. III, 91 (42).



**Use:** Detection of cobalt, copper, nickel and palladium.

Dicyandiamide consists of leaves or plates which melt at 205° C. The compound is moderately soluble in water and in alcohol but is almost insoluble in ether.

**Preparation:** Boil 500 g. of calcium cyanamide for one-half hour with 1 liter of water and filter. Dicyandiamide separates from the filtrate upon cooling.<sup>1</sup>

**Detection of nickel and copper.** When dicyandiamide is treated with acids, dicyandiamidine is formed; hence, dicyandiamide may be used for the formation of the latter compound as a reagent for copper and nickel.<sup>2</sup>

**Procedure.** To a solution of dicyandiamide add a few drops of hydrochloric acid and heat to boiling. Upon the addition of a solution containing nickel and then a little potassium hydroxide, a yellow crystalline precipitate is formed.

The sensitivity of this test is 1:20,000.

**Detection of cobalt.** Dicyandiamidine, which is formed from dicyandiamide, reacts with cobalt in the presence of potassium hydroxide and sucrose to yield a red to red-violet color. This reaction has been used for the detection of cobalt.<sup>4,5</sup> Nickel and copper interfere.

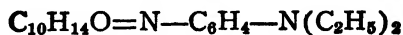
**Detection of palladium.** When a solution of dicyandiamide is added to a 2 per cent solution of palladium chloride, and the mixture allowed to stand, a few irregular clusters of yellow needle-shaped crystals appear at the edge of the drop. No other metals of the platinum group give reactions with dicyandiamide.<sup>3</sup>

1. J. Söll and A. Stutzer, *Ber.* **42**, 4532 (1909).
2. H. Grossmann and B. Schuck, *Ber.* **39**, 3356 (1906).
3. W. F. Whitmore and H. Schneider, *Mikrochemie.* **17**, 279-319 (1935).
4. H. Grossmann and W. Heilborn, *Ber.* **41**, 1878 (1908).
5. H. Grossmann and W. Heilborn, *Chem.-Ztg.* **33**, 841 (1909).

## DIETHYLAMINOPHENYLIMINOCAMPHOR



Mol. Wt. 312.42



**Use:** Detection of mercury.

This reagent is obtained as orange-colored needles from dilute alcohol. It melts at 102.5° C. It is soluble in alcohol, benzene and chloroform.

**Preparation:** *Camphorquinone*. For preparation, see below.

*Diethylaminophenyliminocamphor*. Mix 1.82 g. of camphorquinone and 1.64 g. of *p*-aminodiethylaniline with 25 ml. of absolute alcohol and a little anhydrous sodium sulfate. Reflux on a water bath for three hours. Cool, pour the reaction mixture into water, and recrystallize the product a number of times from dilute alcohol.<sup>1</sup>

**Detection of mercury.** Diethylaminophenyliminocamphor reacts with mercurous or mercuric ions to give a deep violet coloration.<sup>2</sup> This reaction may be used for the detection of small quantities of mercury.

**Procedure.** Soak filter paper in a 0.5 per cent solution of the reagent and dry in air. A drop of a mercury salt solution yields a rose color when applied to this paper. The color vanishes on exposure to ammonia if caused by mercuric ions, or turns black if caused by mercurous ions.

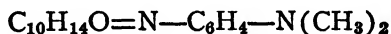
One part of mercuric chloride can be detected in 50,000 parts of water.

1. M. Singh and M. Singh, *J. Indian Chem. Soc.* 12, 768-70 (1935).
2. M. Singh, *J. Indian Chem. Soc.* 15, 402 (1938); *C.A.* 33, 71 (1939).

## DIMETHYLAMINOPHENYLIMINOCAMPHOR

$C_{18}H_{24}ON_2$

Mol. Wt. 284.37



**Use:** Detection of mercury.

This compound is a light brown crystalline substance. It melts at 135.5° C. It is insoluble in water, but is soluble in methyl and ethyl alcohols and benzene.

**Preparation.** *Camphorquinone*: Mix 100 g. of camphor, 80 ml. of acetic anhydride and 80 g. of finely powdered selenium dioxide and heat to boiling with stirring. Heat for 2 hours and add an additional 20 g. of selenium dioxide. Again heat for 2 hours and add 20 g. more of selenium dioxide. Continue heating for 3-4 hours. Cool and almost neutralize with 30 per cent sodium hydroxide, and then make alkaline with a soda solution. Distill with steam and extract the distillate with ether. Recrystallize from dilute alcohol. The yield is increased by adding water to the mother liquor.<sup>1</sup>

*Dimethylaminophenyliminocamphor*: Dissolve equal molecular quantities of camphorquinone and *p*-aminodimethylaniline in absolute alcohol. Add a little anhydrous sodium sulfate and heat the mixture on a water bath with reflux for 3 hours. Evaporate the excess alcohol, cool, and pour into water. Extract the mass which settles with 50-60 per cent alcohol and recrystallize as a light brown, fluffy crystalline mass from 50-60 per cent alcohol.<sup>2</sup>

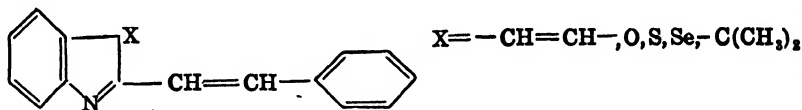
**Detection of mercury.** A 1.0 per cent alcoholic solution of the reagent gives a deep scarlet color with solutions of mercuric salts. This reaction has been used by Singh<sup>3</sup> for the detection of mercuric salts. No reaction is obtained with lead, copper, nickel, cobalt, iron, calcium, barium, cadmium, manganese and magnesium, but bismuth and silver ions yield a faint pink color and a slight white precipitate.

The mercury test may be carried out as a spot test. Soak filter paper in a 0.5 per cent solution of dimethylaminophenyliminocamphor and dry in air. A drop of mercuric salt solution gives a rich pink colored spot which vanishes on exposure to ammonia. This reaction is sensitive to one part of mercuric chloride in 50,000 parts of water. Mercurous nitrate gives a pink edge to the drop, which becomes black on exposure to ammonia. This reaction is of about the same sensitivity as that with mercuric salts.

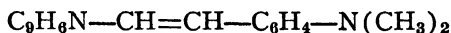
1. H. Rupe and A. Tommasi di Vignano, *Helv. Chim. Acta*, **20**, 1081 (1937).
2. M. Singh, *J. Indian Chem. Soc.* **12**, 219-25 (1935).
3. M. Singh, *J. Indian Chem. Soc.* **15**, 402 (1938); *C.A.* **33**, 71 (1939).

## STYRYL DYES

Heterocyclic bases which have a methyl group, in the  $\alpha$ -position to a tertiary nitrogen atom condense with aromatic aldehydes to form styryl derivatives of the general formula:



The condensation products of *p*-dimethylaminobenzaldehyde, such as *p*-dimethylaminostyrylquinoline:



are yellow compounds which yield red to violet salts with an equivalent amount of an acid. The intense color of the latter is due to the existence of a tautomeric form. With an excess of acid, a salt is formed with a second nitrogen atom. This prevents tautomerization which results in the disappearance of the red color and the reappearance of the yellow color. If a styryl dye forms a difficultly soluble double salt with a heavy metal halide, the dye behaves as a univalent base and forms red salts, even if the precipitation is carried out from a strongly acid and yellow colored solution. Such reactions are used for the detection of silver, gold, palladium, platinum, copper, mercury, tin, cadmium, cobalt, iron, bismuth and manganese. This reaction has also been applied as a very sensitive test for the detection of zinc salts, since the latter form in the presence of iodide or thiocyanate, double salts with organic bases. The test is carried out as follows, using different styryl dyes:

**Procedure.** To 1 ml. of a 0.2 N hydrochloric acid solution of a zinc salt, add a 0.1 per cent alcoholic solution of the styryl base, and then mix with 3 drops

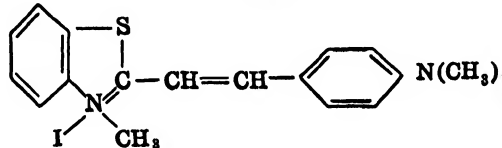
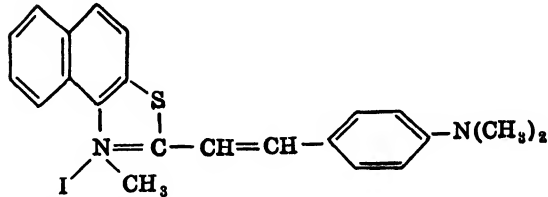
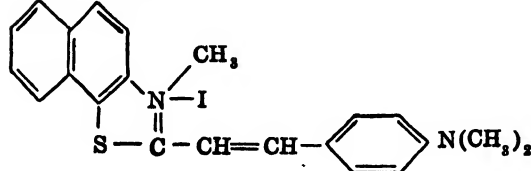
of a 20 per cent solution of potassium thiocyanate. Compare the color reaction with that of a zinc-free blank. The color of the blank is yellow to orange, while the solution containing zinc yields a red to violet color. The results of this reaction are shown in Table 107.

TABLE 107.—REACTION OF STYRYL DYES WITH ZINC

Reagent	Limiting Concentration
$C_6H_5N-CH=CH-C_6H_4-N(CH_3)_2$	1:10,000
$C_{12}H_9N-CH=CH-C_6H_4-N(CH_3)_2$	1:10,000,000
$C_7H_4NS-CH=CH-C_6H_4-N(CH_3)_2$	1:50,000
$C_{11}H_6NS-CH=CH-C_6H_4-N(CH_3)_2$	1:10,000,000

Quaternary salts of the styryl dyes have also been prepared and used for the detection of various metals. The red alcoholic solution of the quaternary salts are similarly changed through an excess of acid to a yellow color. The results obtained with a few thiazolstyryl dyes are shown in Table 108.

TABLE 108. DETECTION OF ZINC WITH THIAZOLSTYRYL DYES

Reagent	Limiting Concentration
	1:500,000
	1:10,000,000
	1:10,000,000

Styryl dyes, which are useful for the detection of metals, are prepared by condensing *p*-dimethylaminobenzaldehyde with quinaldine,  $\beta$ -naphthoquinaldine,  $\alpha$ -methylbenzothiazol,  $\alpha$ -methyl- $\alpha$ -naphthothiazol, and  $\alpha$ -methyl- $\beta$ -naphthothiazol or their methiodides. The general method is as follows:

**Preparation:** Mix equal molecular quantities of the desired base and *p*-dimethylaminobenzaldehyde with 1 per cent of anhydrous zinc chloride, and



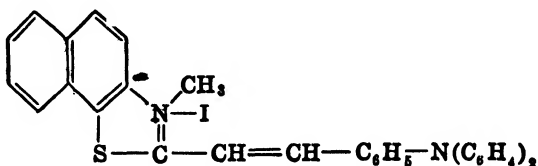
heat for about 2 hours at 200° C. Allow to cool and warm the powdered melt for a few minutes with a dilute sodium hydroxide solution. Allow to cool, filter, and recrystallize the product twice from dioxan.

To prepare the quaternary salts, heat the corresponding methiodides with the equivalent quantity of *p*-dimethylaminobenzaldehyde for an hour in an alcoholic solution with the addition of 0.25-0.5 moles of piperidine. Allow the mixture to cool, filter off the dye with suction, and then wash with alcohol and ether.

### ***p*-DIMETHYLAMINOSTYRYL- $\beta$ -NAPHTHOTHIAZOLE METHIODIDE**

$C_{22}H_{21}N_2SI$

Mol. Wt. 472.37



**Use:** Detection of zinc.

*p*-Dimethylaminostyryl- $\beta$ -naphthothiazole methiodide is the most suitable of the styryl dyes for the detection of zinc. It undergoes a readily observable color change from orange-yellow to violet. Careful attention must be paid to detail in carrying out the test, however, since there are several possible sources of error. The reaction depends upon the concentration of the acid. In strongly acid solutions (greater than 1 N hydrochloric acid) the sensitivity falls very rapidly, and in weakly acid solutions the zinc-free blank also shows a reddish color. The reaction is most suitably carried out in a solution which is about 0.5 N in hydrochloric acid. Further, the sensitivity of the reaction decreases with increase of temperature. For this reason it is best to keep the temperature at about 18° C., or room temperature. Finally, small quantities of iron react similarly, and must be rendered harmless by the addition of oxalic acid. The disturbing influence of traces of copper cannot be eliminated.

**Procedure.** To 0.5 ml. of the neutral or slightly acid solution, not exceeding 0.5 N in hydrochloric acid, add 3 drops of hydrochloric acid containing oxalic acid and cool to 18° C. Then add 2 drops of 0.1 per cent alcoholic solution of *p*-dimethylaminostyryl- $\beta$ -naphthothiazole methiodide and 3 drops of a 20 per cent potassium thiocyanate solution. According to the quantity of zinc present, a rose to violet color appears. This should be compared with a zinc-free blank prepared in a similar manner. In a neutral solution, 0.05  $\gamma$  of zinc can be detected at a concentration of 1:10,000,000, while in a 0.4 N hydrochloric acid solution only 0.2  $\gamma$  of zinc at a concentration of 1:2,500,000 can be detected.

Under the same conditions a number of metals give similar color reactions. These metals, and the sensitivity of their reaction with *p*-dimethylaminostyryl- $\beta$ -naphthothiazole methiodide, are shown in Table 109.

TABLE 109.

Ion	Sensitivity
Silver .....	1:200,000
Gold .....	1:2,000,000
Palladium .....	1:5,000,000
Platinum .....	1:20,000
Copper (ic) .....	1:1,000,000
Mercury (ic) .....	1:1,000,000
Tin (ic) .....	1:500,000
Tin (ous) .....	1:200,000
Cadmium .....	1:10,000
Cobalt .....	1:50,000
Iron (ous) .....	1:25,000
Bismuth .....	1:5,000
Manganese .....	1:1,000

Most other metals in concentrations up to 1 per cent give no positive reaction.

Wenger and co-workers,<sup>2</sup> who have studied the various reactions proposed for zinc, recommend *p*-dimethylaminostyryl- $\beta$ -naphthothiazole methiodide as a suitable reagent for a micro-, and macrochemical test and for a drop reaction. The sensitivity is given as 0.05 $\gamma$  of zinc in 0.5 ml.

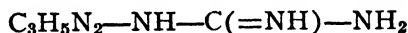
1. P. Krumholz and E. Krumholz, *Mikrochemie*, **19**, 47-57 (1935); *C.A.* **30**, 43 (1936).
2. P. Wenger, R. Duckert and D. Rieth, *Helv. Chim. Acta*, **25**, 406-15 (1942); *C.A.* **36** 6438 (1942).

## ETHYLENE BIGUANIDE



Mol. Wt. 127.11

Beil. Ref. XXIV, 3.



**Use:** Reaction with copper and nickel.

Ethylene biguanide is a syrupy liquid which decomposes upon heating. The hydrochloride is a crystalline solid which is readily soluble in water.

**Preparation:** Ethylene Biguanide is prepared by melting together ethylenediamine hydrochloride with dicyandiamide at 140-150° C.<sup>1</sup>

**Reaction with copper and nickel.** Dubsky, Langer, and Strnad<sup>2</sup> have prepared the following copper and nickel salts of ethylene biguanide.

TABLE 110.

Metal	Description	Formula
Copper .....	Rose color	$(\text{C}_4\text{H}_5\text{N}_5)_3\text{Cu} \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
Nickel .....	Orange-yellow	$(\text{C}_4\text{H}_5\text{N}_5)_3\text{Ni} \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

1. E. Dittler, *Monatsh.* **29**, 647 (1908).
2. J. V. Dubsky, A. Langer, and M. Strnad, *Collection Czechoslov. Chem. Commun.* **10**, 103-16 (1938); *C.A.* **32**, 4472 (1938).

**GLYOXALIN**

Synonym: Imidazol

 $C_3H_4N_2$ 

Mol. Wt. 68.08

Beil. Ref. XXIII, 45.

**Use:** Detection of cobalt.

Glyoxalin is a crystalline solid melting at 90° C. It is readily soluble in water, alcohol and chloroform, but is only slightly soluble in ether. The compound reacts as a weak base.

**Preparation:** Place 200 g. of powdered *d*-tartaric acid in a 2-liter, 3-necked flask, and fit with a thermometer, a stirrer, and a 1-liter dropping funnel. Then add successively 432 ml. of nitric acid (d. 1.42) and 432 ml. of fuming nitric acid (d. 1.50), and stir 5-10 minutes, or until solution is complete or nearly so. Now add slowly from the dropping funnel 800 ml. of sulfuric acid (d. 1.84). When the temperature of the reaction mixture reaches 38° C., surround the flask with ice water, and continue the addition of the acid at such rate that the temperature remains at 38-43° C. After all the acid has been added, allow the mixture to stand in a cool place for 3 hours.

Break up the crystalline mass with a glass rod, and collect on a filter cloth or glass wool on a Buchner funnel. Press as dry as possible, and transfer in portions to a 4-liter beaker containing 3 liters of finely crushed ice. Stir well with each addition until each portion is dissolved. Pour the cold solution immediately into a previously assembled apparatus, which consists of a 5-liter, 3-necked flask immersed in a tub of ice-salt mixture, and fitted with a stirrer, dropping funnel, and a thermometer for reading low temperatures. Neutralize to Congo red by the addition of 600-700 ml. of ammonium hydroxide (d. 0.90) at such rate that the temperature never exceeds -5° C. About 3-4 hours is required for this operation. Finally, add an additional 100 ml. of ammonium hydroxide.

During the neutralization, prepare a solution of hexamethylenetetramine by the careful addition of 520 ml. of formalin (d. 1.08) to 500 ml. of ammonium hydroxide (d. 0.90). Keep the temperature below 20° C. by external cooling during this operation. Finally, chill the solution to 0° C., and add dropwise to the cold ammoniacal solution of the tartaric acid dinitrate. The temperature must not exceed 2° C. Allow the mixture to stand overnight. Filter the mixture, add 100 ml. of alcohol to the filtrate, and acidify to Congo red by the careful addition of about 400 ml. of hydrochloric acid (d. 1.19). Cool in an icebox for 4-5 hours and collect the imidazole-4,5-dicarboxylic acid on a Buchner funnel. Transfer the solid to a 1-liter beaker, stir with 400-500 ml. of water, and again filter. Wash on the funnel successively with three 150-ml. portions of water,

two 75-ml. portions of methyl alcohol, and finally with 75 ml. of ether. Dry in air.

Divide the solid into 2 portions, and mix each intimately with about 0.5 g. of copper-chromium oxide catalyst or powdered copper oxide, and transfer the resulting mixture to a 250-ml. Claisen flask having a modified side arm. Place the receiving flask loosely over the side arm, and heat the flask gently with a free flame. After a small amount of material has distilled at 95-100° C., the temperature rises sharply to 260° C., and imidazole distills at 262-264° C. Purify by dissolving in 60-70 ml. of benzene and boiling for a few minutes with 2-3 g. of decolorizing charcoal. Filter through a preheated Buchner funnel, and cool the filtrate to 10° C. for 2 hours.<sup>1,2,3</sup>

**Detection of cobalt.** Fischer <sup>4</sup> recommends glyoxalin as a very delicate reagent for cobalt, with which it reacts to give a violet-blue precipitate.

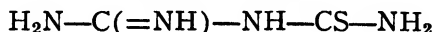
1. R. Behrend and J. Schmitz, *Ann.* **277**, 338 (1894).
2. G. Wyss, *Ber.* **10**, 1366 (1877).
3. H. R. Snyder, R. Q. Handrick and L. A. Brooks, *Organic Synthesis* **22**, 65.
4. E. J. Fischer, *Wiss. Veroffentl. Siemens-Konzern.* **4**, 171-87 (1925); *Chem. Zentr.* **II**, 470 (1926).

## GUANIDYLTHIOUREA

C<sub>2</sub>H<sub>6</sub>N<sub>4</sub>S

Mol. Wt. 118.13

Beil. Ref. III, 191.



**Use:** Detection and determination of silver.

**Preparation:** Prepare the free base by heating dicyandiamide for 1 day with a saturated solution of hydrogen sulfide at 60-70° C. Precipitate with ammonium oxalate and oxalic acid, dissolve in a little hot water, and decompose with barium hydroxide. Remove barium with carbonic acid, filter, and evaporate until crystals appear.<sup>1</sup> Use as guanidylthiourea carbonate.

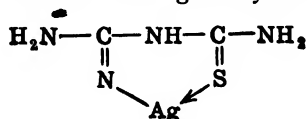
Guanidylthiourea is also prepared by heating thiophosgene with 3 moles of thiourea at 100-110° C.<sup>2</sup>

**Detection and determination of silver.** Silver is detected by the yellow color which is formed when guanidylthiourea carbonate reacts with solutions of silver salts. This color is obtained with as little as 0.4 p.p.m. of silver ion, and attains a maximum within 5 minutes. When stabilized with gum ghatti, the color remains unchanged for 1 week. The optimum conditions for the color reactions are obtained in 0.1 N sodium hydroxide solution with 0.1 N ammonium hydroxide. In the absence of ammonium hydroxide a turbidity develops in solutions in which the silver concentration exceeds 5 p.p.m. The color does not obey Beer's law, and is not affected by temperature changes over the range 20-30° C. Color matching is more sensitive in the range of 1-12 p.p.m. of silver. If the solution is allowed to stand for some time, a brown precipitate of colloidal silver settles out.<sup>3</sup>

Copper, mercury, lead, cadmium, and bismuth interfere and should be absent.

The analysis of silver materials is performed by separating the silver as the chloride in a hot solution, followed by centrifuging and dissolving the precipitate in ammonia. The soluble complex is then treated with the reagent and the color is developed and compared with that of standard silver solutions. The color is independent of the ammonia concentration provided the latter is at least 0.05 N. Results are excellent.

The character of the colored product formed when guanidylthiourea and silver salts react has not been definitely established, but an ultramicroscopic examination has revealed that the reaction mixture contains colloidal particles, and photomicrographs indicate that the compound is not silver sulfide and is not a compound with thiourea. While there is some likelihood that the color is due to colloidal silver, it seems probable that the reaction product consists of a suspension of a compound of silver with guanidylthiourea of the type:



This seems more probable since guanidylthiourea contains the  $=\text{N}-\text{H}$  group and an adjacent S atom, which, according to Feigl, makes possible the formation of a stable, 6-membered ring by coordinate linkage.<sup>3</sup>

1. E. Bamberger, *Ber.* 16, 1460 (1883).
2. B. Rathke, *Ber.* 11, 962 (1878).
3. T. B. Crumpler and E. B. Claiborne, *Va. J. Sci.* 3, No. 1, 29-30 (1942); *C.A.* 36, 3117 (1942).

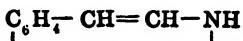
## INDOLE

Synonym: Benzopyrrole

$\text{C}_8\text{H}_7\text{N}$

Mol. Wt. 117.14

Beil. Ref. XX, 304.



**Use:** Detection of gold and nitrite.

Determination of nitrite and potassium.

Indole occurs principally in coal tar, from which it is obtained by fractional distillation. It consists of colorless to yellowish scales, having an intense fecal odor. It melts at  $52^\circ\text{C}$ . and boils at  $253-254^\circ\text{C}$ . with decomposition. It is soluble in hot water, alcohol, ether and petroleum benzene.

**Preparation:** Indole may be prepared by mixing nitrocinnamic acid with 10 parts of powdered KOH, adding iron filings, and then heating until the mass is melted.<sup>1</sup>

**Detection and determination of nitrites in water.** Nitrites may be detected by the red color which forms when an alcoholic solution of indole is

added to an acid solution containing nitrites.<sup>2-5</sup> The following procedure has been suggested by Dane.<sup>2</sup>

**Reagent.** Dissolve 0.02 g. of indole in 150 ml. of 95 per cent ethyl alcohol.

**Procedure.** Add 2-5 ml. of the reagent to a little of the solution to be tested and acidify with 1:2 sulfuric acid. A pink to red color appears in less than 1 minute if nitrites are present, and the concentration of the nitrite may be determined colorimetrically. The reaction is sensitive to 1 part of nitrite in 2,500,000 parts of solution.

Inada<sup>5</sup> performs the test as follows:

**Procedure.** Add 4 drops of a 1 per cent indole solution and two drops of concentrated sulfuric acid to 2 ml. of the solution to be tested. A red color appears if nitrite is present. The sensitivity of this reaction is 1:4,000,000.

**Determination of potassium.** Potassium has been determined colorimetrically by an indirect method which depends upon measuring the color obtained by the reaction between indole and the nitrite contained in the precipitate of potassium cobaltinitrite.<sup>6</sup> Results reported are not very satisfactory.

**Detection of gold.** Gold is detected with indole in a manner similar to that with pyrrole.<sup>7,8</sup>

1. A. Bayer and A. Emmerling, *Ber.* 2, 680 (1869).
2. A. Dane, *Bull. soc. chim.* 9, 354-5 (1911); *C.A.* 5, 2379 (1911).
3. O. Buijwid, *Chem.-Ztg.* 18, 364 (1894).
4. L. Rosenthaler and V. Jahn, *Apoth. Ztg.* 265 (1915).
5. Inada, *Beitr. Chem. Physiol. Path.* 7, 475 (1903).
6. F. Alten, H. Weiland, and B. Kurmies, *Z. Pflanzenernahr Dungung Bodenbk.* 32A, 171-82 (1933); *C.A.* 28, 1298 (1934).
7. P. Saccardi, *Ann. chim. applicata.* 25, 157 (1935); *C.A.* 29, 6173 (1935).
8. G. Giuliani, *Gazz. chim. ital.* 64, 894-6 (1934); *C.A.* 29, 3520 (1935).

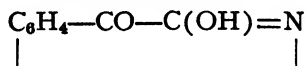
## ISATIN

Synonym: Isatinic acid anhydride

$C_8H_5O_2N$

Mol. Wt. 147.13

Beil. Ref. XXI, 432.



**Use:** Detection of copper and silver.

Isatin consists of yellowish-red, bitter crystals. It melts at 200-201° C. It is slightly soluble in cold water and somewhat more soluble in hot water. It is soluble in alcohol and ether, and also in solutions of alkali hydroxides with which it forms a violet color.

**Preparation:** Mix 100 g. of finely powdered indigo with 300 ml. of boiling water to form a paste and heat to boiling. Then add a mixture of 50 ml. concentrated nitric acid and 10 ml. of water from a dropping funnel at such rate

that the addition is complete in about 20 minutes (1 or 2 drops per second). Stir well during the addition of the nitric acid. After the acid has all been added, boil for about 2 minutes, and then pour about half the liquid into a second vessel and add a liter of boiling water to each portion. Boil for 5 minutes, and decant from the tarry material through a large fluted filter paper previously moistened with water. Add another liter of hot water to each vessel, boil and filter as before. Evaporate the combined filtrates to about 1500 ml. and again filter if more of the tarry material appears. Allow to cool and filter. Redissolve the residue in the smallest quantity of boiling water, and allow the liquid to cool somewhat to permit the tarry material to separate. Filter and evaporate the filtrate until crystals of isatin nearly cover the surface. Then cool and filter off the red crystals. Purify these crystals by dissolving in potassium hydroxide solution, and then adding concentrated hydrochloric acid to the clear liquid as long as a black precipitate is formed. Filter the liquid and precipitate the purified isatin from the filtrate with additional hydrochloric acid. Again filter and recrystallize from water.<sup>1,2</sup>

**Detection of silver and copper.** The action of free isatin in a neutral or acid solution corresponds to the keto-lactim structure, but in alkaline solutions, and in the formation of metallic compounds, its behavior corresponds to an enol-lactim structure. The only metallic compounds which are of analytical value are the silver and copper salts, which separate from the reaction mixture as characteristic crystals. Their formation has been used by Menke<sup>2</sup> for the microchemical detection of silver and copper.

When isatin is allowed to stand for a time in contact with aqueous solutions of an alkali, the compound adds waters to form the alkali salt of isatinic acid. Even low concentrations of alkali retard the formation of isatinic acid and so a solution of 0.5 g. isatin in 100 ml. of 5 per cent ammonia is used to form the silver and copper salts. The precipitate of the silver compound appears as red, star-shaped bundles of crystals. The formation of this compound offers no advantages over silver chloride or silver chromate as a microchemical test for silver.

When cuprous oxide, cuprous chloride, cuprous iodide, or cuprous thiocyanate is added to a solution prepared by dissolving 0.5 g. of isatin in 100 ml. of 5 per cent ammonia, star-shaped, almost colorless crystals are formed. Other metals do not give characteristic precipitates.

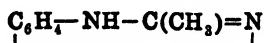
1. J. Erdmann, *prakt. Chem.* 24, 11 (1841).

2. J. B. Menke, *Rec. trav. chim.* 42, 199-203 (1923); *C.A.* 17, 3653 (1923).

**2-METHYLBENZIMIDAZOLE**      Synonym: Ethenyl-*o*-phenylenediamine

$C_8H_8N_2$

Mol. Wt. 132.14      Beil. Ref. XXIII, 145(36).



**Use:** Reactions with silver and mercury.

2-Methylbenzimidazole is obtained as a crystalline compound from water. It melts at 172-174° C. It is easily soluble in alcohol, ether and boiling water.

**Preparation:** Place 54 g. of *o*-phenylenediamine in a 500-ml. flask and add 45 g. of acetic acid. Heat the mixture on a water bath at 100° C. for 2 hours. Cool, and add a 10 per cent sodium hydroxide solution slowly and with thorough mixing until the mixture is just alkaline to litmus. Filter with suction, using ice-cold water to rinse the material out of the reaction flask. Press the crude material on the filter to remove water, and then wash with about 50 ml. of cold water. Dissolve the solid in 750 ml. of boiling water, and digest the solution for 15 minutes with 2 g. of decolorizing carbon. Filter rapidly through a heated filter, and cool the filtrate to 10-15° C. Filter off the crystals which form, and wash with 50 ml. of cold water. Dry at 100° C.<sup>1,2,3</sup>

**Reaction with silver and mercury.** A precipitate of  $C_8H_7N_2Ag$  is obtained when a 5 per cent alcoholic solution of 2-methylbenzimidazole is added to an ammoniacal solution of silver nitrate, and the mixture treated with twice its volume of alcohol. The mercury salt ( $C_8H_7N_2HgCl$ ) is prepared in a similar manner.<sup>4</sup>

1. A. Ladenburg, *Ber.* **8**, 677 (1875).
2. O. Hinsberg and F. Funcke, *Ber.* **27**, 2189 (1894).
3. *Organic Synthesis*, Collective Volume, II, p. 66, John Wiley, New York.
4. F. Feigl and H. Gleich, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).

## NITROAMINOGUANIDINE



Mol. Wt. 119.05



**Use:** Determination of nickel.

Nitroaminoguanidine is a white crystalline solid. It melts at 190° C. with decomposition. It is insoluble in most organic liquids, but a saturated aqueous solution at 20° C. contains 0.34 per cent of the solid, and at 70° C., 3 per cent of the reagent.

**Preparation.** *Nitroguanidine:* Dissolve 80 g. of guanidine nitrate in small portions in 100 ml. of concentrated sulfuric acid, keeping the temperature below 25° C., and pour the resulting solution into 600 ml. of ice water. Collect the precipitate which forms by filtration, and purify by recrystallizing twice from water.<sup>1</sup>

*Nitroaminoguanidine:* Place 32.53 g. of hydrazine sulfate in a 2-liter flask with 200 ml. of distilled water and 500 ml. of 1 N ammonium hydroxide. When solution is complete, add 26 g. of nitroguanidine. Heat the mixture to 50-60° C. for 1 hour, and rapidly evaporate the liquid to about one-third of its original volume. Cool, filter and wash with water. Dissolve the residue in boiling water containing a little decolorizing charcoal, filter, cool the filtrate, and collect the precipitate by filtration.<sup>2</sup>



**Determination of nickel.** Phillips and Williams<sup>2</sup> have suggested the use of nitroaminoguanidine as a reagent for the quantitative precipitation of nickel. This reagent possesses the advantage over dimethylglyoxime that it is comparatively soluble in water. The following procedure is recommended for precipitating nickel.

**Procedure.** Place 5 ml. of a solution of nickel sulfate, containing about 0.09 g. of nickel, in a 250-ml. beaker and dilute with 100 ml. of hot water. Add 5 ml. of 1 N ammonium hydroxide, and add a solution of 0.5 g. of nitroaminoguanidine dissolved in 50 ml. of hot water. Boil gently for 15-20 minutes, filter through a weighed crucible, wash with hot water, and dry at 110° C. The precipitate contains 18.75 per cent nickel and corresponds in composition to the formula,



Experiments show that the nickel is completely precipitated by using this procedure.

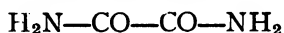
1. T. L. Davis, A. A. Ashdown and H. R. Couch, *J. Am. Chem. Soc.* **47**, 1063 (1925).
2. R. Phillips and J. F. Williams, *J. Am. Chem. Soc.* **50**, 2469 (1928).
3. P. L. Hibbard, *Ind. Eng. Chem., Anal. Ed.* **10**, 615-8 (1938).

## OXAMIDE



Mol. Wt. 88.05

Beil. Ref. II, 545.



**Use:** Detection of nickel.

Oxamine is obtained as needle-like crystals. It sublimes when heated in an open vessel. It is slightly soluble in water, and somewhat less soluble in alcohol.

**Preparation:** Place 16 g. of dry ethyloxalate in a dry U-tube immersed in a bath of ice and salt. Add 40 ml. of absolute alcohol, and then pass anhydrous ammonia through the mixture for 20 minutes. Separate the crystals and wash with water and alcohol. Recrystallize from hot water.<sup>1</sup>

**Detection of nickel.** Nickel may be detected by the yellow coloration which appears when a dilute solution of a nickel salt is added to oxamide, and the resulting mixture treated with sodium or potassium hydroxide. The reagent causes a very intense color.<sup>2</sup> The test is performed as follows:

**Procedure.** Place about 1 ml. of powdered oxamide in a test tube and add 1 ml. of nickel sulfate solution. Bring the mixture to a boil and add a little concentrated sodium hydroxide solution. A yellow color appears immediately, but this soon fades on standing. Boiling with sodium hydroxide is to be avoided as the reagent undergoes cleavage.

The test may be modified by mixing equal quantities of finely ground barium hydroxide or calcium hydroxide and oxamide. This eliminates the use of sodium hydroxide.

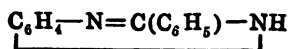
The test is less sensitive than that of Tschugaeff, using dimethylglyoxime, and the reaction is not quantitative.

The reaction fails in the presence of cations which form colored hydroxides. Nickel and cobalt can be precipitated together as sulfides, filtered, the sulfides dissolved in aqua regia, and cobalt precipitated as potassium cobaltic nitrite. After filtering the cobalt compound, the filtrate is tested as above. If the filtrate is colored, boil with sulfuric acid.

1. I. K. Phelps, L. H. Weed, and C. R. Housum, *Am. J. Sci.* **24**, 479 (1907).
2. J. Liska, *Chem. Listy.* **23**, 402-3 (1929); *C.A.* **23**, 5430 (1929).

## 2-PHENYLBENZIMIDAZOLE

$C_{13}H_{10}N_2$  Mol. Wt. 194.21 Beil. Ref. XXIII, 230(61).



**Use:** Reaction with mercury and silver.

This compound is obtained in the form of needle-like crystals from water. It melts at 280° C. It is moderately soluble in ethyl alcohol, and is only slightly soluble in water, chloroform and benzene, but dissolves readily in acetic acid.

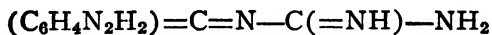
**Preparation:** 2-Phenylbenzimidazole is obtained by heating *o*-phenylenediamine hydrochloride with benzoin.<sup>1</sup>

**Reaction with silver and mercury.** Feigl and Gleich<sup>2</sup> have prepared the silver and the mercury salts of 2-phenylbenzimidazole. These correspond to the formula  $C_{13}H_9N_2Ag$  and  $C_{13}H_9N_2HgCl$ . The silver salt is precipitated when a strongly ammoniacal solution of silver nitrate is mixed with the reagent and twice its volume of alcohol.

1. F. R. Japp and A. N. Meldrum, *J. Chem. Soc.* **75**, 1043 (1899).
2. F. Feigl and H. Gleich, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928)

## *o*-PHENYLENEBIGUANIDE

$C_8H_9N_5$  Mol. Wt. 175.15 Beil. Ref. XXIV, 118.



**Use:** Reactions with antimony, bismuth, copper, mercury, silver and zinc.

This compound is obtained as yellow leaves which melt at 742° C. It is easily soluble in alcohol, acetone, and hot water, but is only slightly soluble in ether, and is not soluble in benzene. The solutions are yellow and react alkaline.

**Preparation:** *o*-Phenylenebiguanide is prepared by heating *o*-phenylenediamine hydrochloride with dicyandiamide in alcohol for a long time in a tube at 105° C.<sup>1</sup>

**Reaction with metals.** *o*-Phenylenebiguanide reacts with the salts of a number of metals to yield colored compounds.

Dubsky, Langer, Strnad<sup>2</sup> have prepared a number of these salts, and their results are reported in Table 111.

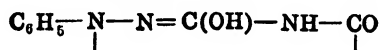
TABLE 111.

Metal	Description	Formula
Cobalt .....	Grayish-brown	$\text{Co}(\text{C}_8\text{H}_8\text{N}_8)_2 \cdot 2\text{H}_2\text{O}$
Cobalt .....	Brick-red	$\text{Co}(\text{C}_8\text{H}_8\text{N}_8)_3$
Nickel .....	Chocolate	
Nickel .....	Reddish-brown	$(\text{C}_8\text{H}_8\text{N}_8)_2\text{Ni} \cdot \text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Copper .....	Olive-brown	$\text{Cu}(\text{C}_8\text{H}_8\text{N}_8)_2 \cdot \text{H}_2\text{O}$ $+ \text{Cu}(\text{C}_8\text{H}_8\text{N}_8)_2 \cdot 3\text{HC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$
Copper .....	Clear green	$(\text{C}_8\text{H}_8\text{N}_8)_2 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$
Zinc .....	Light yellow	$\text{Zn}(\text{C}_8\text{H}_8\text{N}_8)_2 \cdot 2\text{H}_2\text{O}$

Silver gives a yellow precipitate; mercuric ions a rose precipitate; copper, a yellowish-green precipitate; bismuth, a reddish precipitate; antimony a rose precipitate; and zinc a yellowish-brown precipitate.

1. R. Ziegelbauer, *Monatsh.* 17, 653 (1896).
2. J. V. Dubsky, A. Langer, and M. Strnad, *Collection Czechoslov. Chem. Commun.* 10, 103-16 (1938); *C.A.* 32, 4472 (1938).

**PHENYLURAZOLE**      Synonym: 1-Phenyl-3-hydroxyl-1,2,4-triazolone-5  
 $\text{C}_8\text{H}_7\text{O}_2\text{N}_3$       Mol. Wt. 177.14      Beil. Ref. XXVI, 193 (57).



**Use:** Detection of mercury.

Phenylurazole is obtained as leaves or needles by crystallization from water. It melts at 262-63° C. It is slightly soluble in cold water, or alcohol, and dissolves readily in solutions of alkalis with the formation of a red color.

**Preparation:** Mix 1 part of phenylhydrazine hydrochloride with 2 parts of urea and heat for 4-5 hours at 160° C. A clear molten mass is obtained which solidifies on cooling. Purify by recrystallizing twice from hot water.<sup>1</sup>

**Detection of mercury.** Phenylurazole reacts with mercury salts in the presence of sodium acetate to yield a beautiful peach-blossom red precipitate. This reaction is sensitive to 1 part of mercury in 50,000 parts of solution.<sup>2,3</sup>

1. A. Pinner, *Ber.* 20, 2360 (1887).
2. F. Feigl, *Z. angew. Chem.* 39, 393 (1926); *C.A.* 20, 1770 (1926).
3. J. V. Dubsky, *Chem. Obzor.* 8, 71-2, 93-5 (1933); *C.A.* 28, 5361 (1934).

**PYRROLE**      Synonym: Azole, imidol  
 $\text{C}_4\text{H}_5\text{N}$       Mol. Wt. 67.09      Beil. Ref. XX, 159.



**Use:** Detection of gold, selenious acid and silicic acid.

Determination of chromate, gold, iodate, mercury, selenious acid, silicic acid and vanadium.

Pyrrole is a colorless liquid when freshly distilled, but after a few days it turns yellow and finally becomes dark brown. It boils at  $131^{\circ}\text{C}$ . and has a sp. gr. of 0.948. It is insoluble in water but dissolves readily in alcohol, benzene and ether. It is quite poisonous, causing central paralysis.

**Preparation:** Dissolve 15 g. of mucic acid in 15 ml. of 20 per cent ammonia solution, and evaporate to dryness in a porcelain dish. Stir the ammonium mucate with 20 ml. of glycerol in a distilling flask and heat the mixture. The reaction begins at  $170^{\circ}\text{C}$ ., and the major part of the pyrrole distills between  $180^{\circ}$  and  $210^{\circ}\text{C}$ . Dissolve the distillate in a little ether, dry, and fractionally distill. The boiling point of pyrrole is  $131^{\circ}\text{C}$ .<sup>1,2</sup>

**Detection and determination of selenious acid.** Pyrrole is oxidized by selenious acid to give a deep blue coloration, due to the formation of pyrrole blue. In the presence of phosphoric acid the sensitivity of this reaction is about 1:500,000 but in the presence of iron, which catalyzes the oxidation, the sensitivity is increased to 1:12,000,000.<sup>3</sup>

**Procedure.** To 1-2 ml. of selenious acid solution, add 1 ml. of 5 per cent ferric chloride solution and dilute to 10 ml. with phosphoric acid ( $d = 1.85$ ), and add 5-10 drops of 1 per cent pyrrole in alcohol. A blue coloration is a positive test.

If 2 ml. of 8 per cent ammonium molybdate and 10 ml. 1:1 sulfuric acid are used instead of phosphoric acid, the sensitivity is increased to 1:30,000,000, but the reaction is less specific. The above reaction may be made the basis for a colorimetric determination of selenium, but the color fades rapidly.

Selenium tetrachloride and pyrrole react to give a black precipitate or a brown color, which may be used for detecting selenium as the tetrachloride.<sup>4</sup> Selenium can be detected by this reaction at concentrations as low as 1:564,000.

**Detection of silicic acid.** The test for silicic acid consists of the formation of pyrrole blue and bolybdenum blue by the reciprocal action of pyrrole and silicomolybdic acid.<sup>3</sup> The test is carried out as follows:

**Procedure.** Mix 1-2 ml. of the solution to be tested with 2 ml. of 8 per cent ammonium molybdate,  $((\text{NH}_4)_2\text{MoO}_4)$ , and 10 ml. of 1:1 sulfuric acid. Allow to cool, and add 5 drops of 1 per cent alcoholic pyrrole solution. A blue color appears with silicic acid.

The color produced in the above reaction may be used for the colorimetric determination of silicic acid, but the color fades rapidly.

**Reactions.** A number of ions may be detected by means of spot tests developed by Dremlyuk.<sup>5</sup> These tests are based upon the different colors obtained by the oxidation of pyrrole with various oxidizing agents in the presence

of phosphoric acid ( $d = 1.7$ ), and on the different stabilities of the oxidation products so obtained.

In this way gold may be detected in the presence of all anions and cations; <sup>6</sup> vanadium in the presence of molybdenum and tungsten; iodate in the presence of bromate and chlorate; chromate in the presence of permanganate; and mercurous ions in the presence of many other substances.

Pyrrole reacts with auric chloride to form an amorphous, black, and extremely insoluble precipitate. This reaction is sensitive to 1 part of gold in 1,400,000 parts of water.

1. H. Schwanert, *Ann.* **116**, 271 (1860).
2. E. Khotinsky, *Ber.* **42**, 2506 (1909).
3. R. Berg and M. Tettelbaum, *Mikrochem., Emich Festschr.* 23-6 (1930); *C.A.* **25**, 3263 (1931).
4. P. Saccardi and G. Martini, *Chim. ind., agr., biol.* **13**, 210 (1937); *C.A.* **31**, 8429 (1937).
5. R. L. Dremlyuk, *J. Applied Chem. (U.S.S.R.)*, **13**, 157-60 (1940); *C.A.* **34**, 7780 (1940).
6. P. Saccardi, *Ann. chim. applicata*, **25**, 157 (1935).

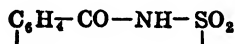
## SACCHARIN

Synonym: Anhydro-*o*-sulfaminebenzoic acid, *o*-sulfobenzimide



Mol. Wt. 183.18

Beil. Ref. XXVII, 168.



**Use:** Detection of thallium.

Saccharin is a white crystalline solid. It dissolves in water, and the resulting solution possesses an intensely sweet taste. It melts at 220° C. It is only slightly soluble in water, but is more soluble in alcohol and in acetone. It is slightly soluble in ether and chloroform.

**Detection of thallium.** Saccharin reacts with thallium salts to form a white crystalline compound which may be used for the detection of the metal. The reaction is sensitive to 20 mg. of thallium per ml. of solution.<sup>1,2</sup>

1. L. Rosenthaler, *Pharm. Zentr.* **74**, 290 (1933).
2. J. C. Munch and J. C. Ward, *J. Am. Pharm. Assn.* **24**, 351-8 (1935); *C.A.* **29**, 5037 (1935).

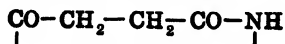
## SUCCINIMIDE

Synonym: 2,5-Diketopyrrolidine



Mol. Wt. 99.09

Beil. Ref. XXI, 369.



**Use:** Detection of fluorine.

Succinimide is a white crystalline solid which melts at 125-127° C. It is soluble in water and somewhat less soluble in alcohol. It is insoluble in ether and chloroform.

**Preparation:** Heat 10 g. of succinic anhydride and 6 g. of urea in a distilling flask. As the temperature rises, the contents of the flask melt and become dark, and ammonia and carbon dioxide are evolved. Upon continuing the heating, a product distilling at about 280° C. is obtained. This solidifies and is recrystallized from anhydrous acetone.<sup>1</sup>

Succinimide may also be prepared by rapidly distilling ammonium succinate.

**Detection of fluorine.** Miller<sup>2</sup> has used mercury succinimide with benzidine for the detection of fluorine.

**Reagent.** Dissolve 1.84 g. of benzidine in glacial acetic acid, dilute to 500 ml. with water. Mix this solution with 500 ml. of 0.02 N mercury succinimide solution.

Mercury succinimide is prepared by dissolving mercuric oxide in a warm concentrated aqueous solution of succinimide. On cooling, the mercury salt crystallizes. Filter and recrystallize from alcohol or water.<sup>3</sup>

**Procedure.** Neutralize the solution to be treated with sodium hydroxide and make just acid with acetic acid. Heat to 50° C. and add an excess of the reagent. A precipitate is obtained with as little as 0.4 mg. of fluorine in 10 ml. of solution.

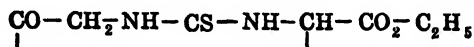
Oxidizing agents and sulfuric and phosphoric acids must be absent.

1. F. L. Dunlap, *Am. Chem. J.* **18**, 336 (1896).
2. C. F. Miller, *Chemist-Analyst*, **26**, 35 (1937).
3. N. Menshutkin, *Ann.* **162**, 171 (1872).

## 2-THIO-5-KETO-4-CARBETHOXY-1,3-DIHYDROPYRIMIDINE

$C_7H_{10}O_3N_2S$

Mol. Wt. 202.21



**Use:** Detection and determination of silver.

This compound is an orange crystalline solid melting at 276-280° C. It is slightly soluble in acetone, acetic acid, chloroform and hot benzene, but it is insoluble in water.

**Preparation:** Suspend 50 g. of ethyl glycinate hydrochloride in 25 ml. of water contained in a separatory funnel, and add 30 ml. of 40 per cent sodium hydroxide solution while shaking and cooling under running water. Saturate the resulting mixture with potassium carbonate, and then extract with four 25-ml. portions of ether. Dry the ether extract over anhydrous potassium carbonate for 24 hours. Filter and wash the residue twice with ether that has been dried over sodium. Cool the filtrate in ice, and add 8 ml. of carbon disulfide

while stirring and cooling in ice. The diethylaminoacetate dithiocarbamate separates as an oil, which then freezes to a white solid. Remove the ether by decantation, and immediately pour on 50 ml. of 99 per cent ethyl alcohol. Next add 2 ml. of carbon disulfide and reflux for 24 hours. Cool with ice and stir well. Filter off the precipitate which forms and evaporate the filtrate to one half its original volume. Filter off the orange red precipitate of the reagent, and purify by recrystallizing from ethylene chlorohydrin. The yield is about 0.3 g.<sup>1,4</sup>

**Detection and determination of silver.** Sheppard and Brigham<sup>1</sup> first prepared 2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine and studied its reaction with a number of metallic ions. As the reagent they employed a 0.03 per cent solution of the compound in acetone, and added 0.5 ml. of this solution to 10 ml. of the solution to be tested. In a neutral solution the following color reactions were observed: silver, purple; cadmium, red; aluminum, red; copper, reddish-blue; iron, yellow; lead, blue; zinc, pink, and manganese and tin, white.

In an acid solution silver salts alone give a purple color. Manganese and tin yield white precipitates and all others cause a yellow color. Thus it will be seen that the reagent is specific for silver in an acid solution. The following procedure is used for making the test:

**Procedure.** To 10 ml. of the solution to be tested, add 1 drop of 4 N nitric acid and 2 drops of a 0.03 per cent acetone solution of the reagent. A pink color is obtained at a silver concentration of 1:5,000,000.

Recently Yoe and Overholser<sup>2</sup> have conducted further studies with this reagent and report these additional reactions in neutral solution: cobalt, manganese, and nickel yield pink colors; mercuric salts a pink precipitate; thallos salts a blue precipitate. In nitric acid solutions, gold and mercurous salts give pink precipitates, and palladium compounds give a slight red precipitate. In a nitric acid-sodium acetate buffered solution the following reactions are obtained: silver a purple color and precipitate; gold and palladium an orange color and precipitate; and mercurous and mercuric salts a pink color and precipitate.

Yoe and Overholser<sup>2</sup> proposed the following method for the colorimetric determination of small quantities of silver.

**Reagents.** *2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine solution:* Dissolve 10 mg. of the reagent in 100 g. of acetone. The freshly prepared solution is slightly more sensitive than those which have been allowed to stand, and consequently new solutions should be prepared at least once each week.

*Sodium acetate-nitric acid solution:* Add 320 ml. of 1 M nitric acid to 200 ml. of 1 M sodium acetate, and dilute to 1 liter with water. This solution has a pH of 1.1, but on diluting 10-fold with water the pH is changed to 2.0.

**Procedure.** Transfer the silver solution to a 100-ml. volumetric flask, add 10 ml. of sodium acetate-nitric acid buffer solution and 0.5 ml. of a 0.2 per cent aqueous solution of gelatin, and then dilute almost to the mark with water. Add 0.6 ml. of the reagent, dilute to the mark with water, and then mix thor-

oughly. Allow to stand for 30-40 minutes and compare the color of the solution with that obtained using standards of known silver concentration.

Mercurous and mercuric ions interfere and must be absent. Cobalt, copper, iron and nickel may interfere unless present in very small concentrations.

The intensity of the colored silver compound, as well as the rate of its development, is markedly influenced by pH of the solution. The reaction rate decreases with decreasing pH, and the color formed may vary from purple to blue depending upon the pH. Despite the decreased reaction rate, a buffer with a low pH value is used because less interference and greater stability of color can be obtained than in solutions of higher acidity. Even at low pH, however, the reproducibility and the stability of the color are unsatisfactory for colorimetry unless small amount of gelatin is present to stabilize the colloidal suspension of the silver compound.

1. S. E. Sheppard and H. R. Brigham, *J. Am. Chem. Soc.* **58**, 1046-48 (1936).
2. J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.* **14**, 148-9 (1942); *C.A.* **36**, 1866 (1942).
3. J. H. Yoe and L. G. Overholser, *Va. J. Sci.* **3**, 304 (1943).
4. J. H. Yoe and G. R. Boyd, *J. Am. Chem. Soc.* **64**, 1511-13 (1942).
5. J. H. Yoe, *Va. J. Sci.* **3**, 9 (1942).





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